

The Kinetics of the Reaction between Phosphorus and
The Halogens

by

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INTRODUCTION.

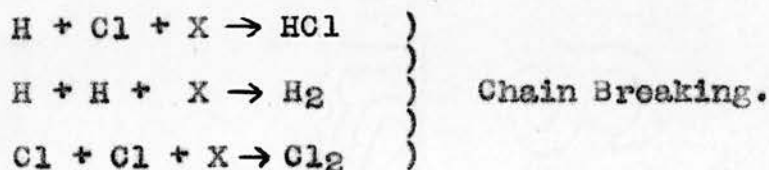
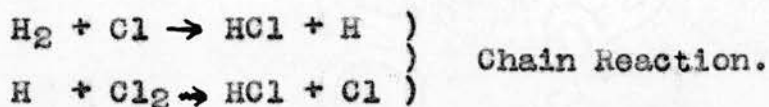
One of the branches of Physical Chemistry which has grown most rapidly in recent years is that which is concerned with the exact mechanisms and velocities of reactions, namely, Reaction Kinetics. The foundations of this subject and also of many other branches of Physical Chemistry are to be found in the classical researches of van't Hoff, Ostwald, and Arrhenius. In particular mention should be made of the famous *Etudes de dynamique chimique* published in 1884 and expounding the fundamental laws of the simple types of reactions. In it van't Hoff stated the laws of mono-, bi-, and trimolecular reactions and gave them a simple kinetic interpretation.

A multitude of papers followed on this publication, and, naturally, they were mainly concerned with examining those reactions which take place in a simple manner and obey the simple laws, i.e. show a normal behaviour. But the number of reactions which are in this sense completely normal is very small so that grave limitations were placed on the study of kinetics. Van't Hoff himself had noted this and the second and third parts of his book are devoted to a detailed study of those reactions which depart from the normal. Among the subjects he studied was that of autocatalysis due to end products, and the catalytic effect of the/

the walls of reaction vessels. He was the first to study minutely the upper pressure limit of the phosphine-oxygen reaction. Unfortunately, interest in these "abnormal" reactions, was lost and only revived when it was found that the number of reactions listed as completely normal was decreasing and not increasing, and when interest in the energy of individual molecules was greatly extended by the application of the Quantum Theory.

The first abnormal reaction to be tackled with any success was that between hydrogen and chlorine. In 1913 Bodenstein found that the quantum yield in the photosynthesis of HCl was of the order of 10^5 . This could not be explained until five years later Nernst¹ put forward the theory which is now accepted and involves the conception known as the "Nernst Chain". This postulates that the chlorine atoms produced by the action of light each react with a hydrogen molecule to give a molecule of hydrogen chloride and a hydrogen atom. This hydrogen atom then reacts with a chlorine molecule to give a molecule of hydrogen chloride and a fresh chlorine atom. The reaction is thus continually using up chlorine atoms but fresh ones are being regenerated, and provided that one chlorine atom has been produced by the action of light and sufficient hydrogen and chlorine are present the only limitation to the course of the reaction is the destruction of hydrogen and chlorine atoms/

atoms, by combination to hydrogen chloride, hydrogen molecules or chlorine molecules or by adsorption on the walls. Later it was realised that combination of the free atoms can only take place in presence of the walls of the vessel or by triple collision with another gas molecule. The excess energy is removed by the third body present.



H or Cl absorbed on wall.

X = wall or molecule of foreign gas.

Unfortunately the only criterion of a chain reaction known at this time was the existence of an abnormally high photochemical yield and so little advance was then made along these lines.

The next advance came from the study of unimolecular reactions the existence of which could not easily be reconciled with the assumption that all activation other than photochemical is due to the collisions between molecules. Perrin² (1919) had considered that all unimolecular reactions are due to absorption of radiation. Such unimolecular reactions as the decomposition of nitrogen pentoxide were/

were exposed to radiation of the theoretical frequency and it was found that no increase in reaction velocity took place. Hence the radiation theory was abandoned.

Christiansen and Kramers^{3, 4} (1924) held that a product molecule in a reaction can activate other molecules by collision and in this way maintain a concentration of activated molecules. The initial number of thermally activated molecules is determined by the Maxwellian distribution and each activated reactant molecule produces an activated product molecule.

This mechanism makes it possible for a reaction to be actually bimolecular but to appear unimolecular. If an inert gas is added the chances of a molecule becoming deactivated are increased and a unimolecular reaction should tend to become bimolecular.

Christiansen and Kramers assumed that the reaction products can only lose their energy to a molecule of the reactant and thus by a not impossible assumption got over the difficulty. In the case of the homogeneous decomposition of nitrogen pentoxide Tolman⁵ (1925) has shown that the reaction is endothermic. Thus the reaction products possess between them less energy than is required to activate a single molecule of N_2O_5 . In the case of this reaction the explanation is not obvious.

Lindemann⁶ (1922) has suggested another theory. He stated that a definite time may have to elapse after/

after activation before reaction takes place. If the molecule suffers another collision before this happens it may be deactivated. In this way a bimolecular reaction can appear unimolecular, but when the pressure is reduced sufficiently it will appear bimolecular.

Let c be the concentration of normal molecules and a that of activated molecules.

$$\text{Rate of activation} = k_1 c^2$$

$$\text{Rate of deactivation} = k_2 a c$$

$$\text{Rate of reaction} = k_3 a.$$

When the rates of production and of destruction of activated molecules are the same

$$k_1 c^2 = k_2 a c + k_3 a$$

$$\therefore \text{Rate of reaction} = k_3 a = \frac{k_1 c^2}{\frac{k_2}{k_3} c + 1}$$

$$\text{If } c \text{ is large } \frac{k_2 c}{k_3} \gg 1$$

$$\text{and rate of reaction} = c \frac{k_1 k_3}{k_2} = K c$$

$$\text{If } c \text{ is small } 1 \gg \frac{k_2 c}{k_3}$$

$$\text{and rate of reaction} = k_1 c^2$$

This pressure effect was looked for and found.

Conclusive evidence of the existence of chain reactions was afforded by a study of negative catalysis. Christiansen⁴ had suggested in 1924 that each molecule of inhibitor acts by breaking reaction chains or preventing their formation. If these chains are/

are of considerable length then a minute quantity of inhibitor is going to have a very large effect.

Experimental evidence was supplied by the work of Bäckström^{7.8.9.10.} on reactions in liquids. He studied the photochemical oxidation of benzaldehyde, heptaldehyde, and sodium sulphite solutions by gaseous oxygen, and concluded from the yields obtained that they were chain reactions. Small traces of inhibitors e.g. anthracene for benzaldehyde and various alcohols for sodium sulphite, markedly reduce the yield and hence the length of the chains. This research was extended to reactions occurring in the dark with similar results. In this case there was no question of the negative catalysis being caused by the destruction of a positive catalyst initially present.

This work established a further criterion for a chain reaction, namely:- If in a homogeneous reaction, the addition of small quantities of a foreign substance produces a marked inhibitive effect on the rate of reaction, and there is no possibility of there having been destruction of a positive catalyst, then the reaction must proceed by a chain mechanism.

Although this investigation was carried out with liquids the conclusions were of importance with regard to gas reactions. Here there are several reactions which can only be dealt with by the use of chains. Mention may be made of the hydrogen-oxygen, the/

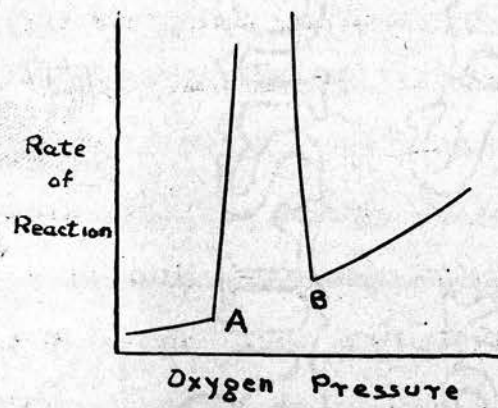


Figure I

the phosphorus-oxygen, and the phosphine-oxygen reactions, all of which could be formulated simply as regards reactants and final products but had baffled all attempts to elucidate their mechanism.

The phosphorus-oxygen reaction forms one of the best illustrations of the uses of the chain theory. The glow of phosphorus in presence of oxygen had been studied as early as the days of Boyle. An advance was made when the study was extended to the reaction between phosphorus vapour and oxygen. It was established, that for a definite temperature and pressure of phosphorus slow reaction with oxygen takes place until the oxygen pressure is raised to a certain value, pt A fig. I. Explosion then occurs and the reaction is explosive for all oxygen pressures between A and B. For oxygen pressures greater than that at B a non-explosive reaction is again obtained. At very low pressures of oxygen no measurable oxidation can be detected. The occurrence of an explosion is indicated by a flash and the oxygen pressures at A and B are known as the upper and lower explosion limits. These pressure limits are extremely sensitive to presence of foreign gases and to the shape and size of the reaction vessel. The upper limit was discovered by Berthollet in 1797 and the lower limit by Joubert¹¹ in 1874.

Various theories had been put forward but the reaction was first shown to be a chain reaction when/

when Bäckström carried out the researches mentioned above. He worked with solutions of phosphorus in heptane and shook them up with oxygen gas observing the amount of oxygen used. Such experiments are quite inconclusive as to mechanism and do not tell whether reaction is in the gaseous or the liquid phase.

Chariton and Walta¹² showed that argon lowered the lower limit, and Semenoff^{13.14} repeated this work and demonstrated that the diameter of the containing vessel also had an effect. He found experimentally the following expression for the lower limit

$$P_{P_4}^{\frac{1}{2}} \cdot P_{O_2} \left(1 + \frac{P_x}{P_{O_2} + P_{P_4}} \right) d^2 = \text{constant.}$$

d = diameter of vessel.

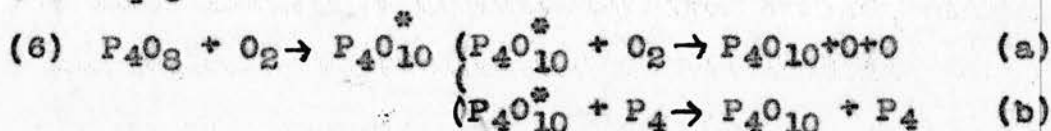
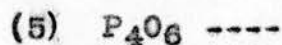
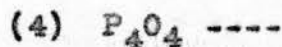
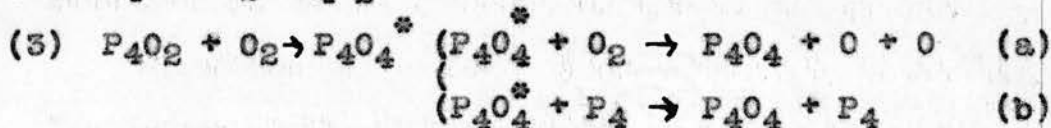
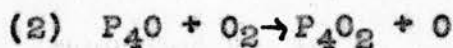
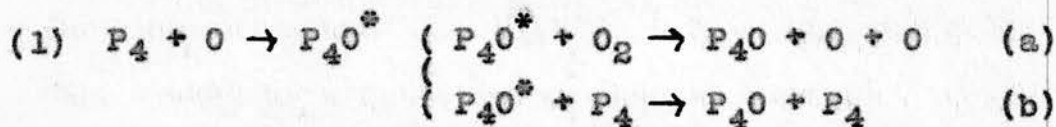
P_{P_4} , P_{O_2} , P_x = pressures of P_4 , O_2 and inert gas.

Semenoff^{13.14.15.16} then suggested that the oxidation of phosphorus was a chain reaction with oxygen atoms and phosphorus oxide molecules as chain carriers, the chains being broken at the lower limit by deactivation of the chain carriers on the walls of the containing vessel. He produced the formula

$$P_{P_4} \cdot P_{O_2} \left(1 + \frac{P_x}{P_{O_2} + P_{P_4}} \right) d^2 = \text{constant.}$$

for the lower limit from the general equations characterising chain reactions. In developing his equations he assumed that the initial oxidation is due to oxygen atoms in equilibrium with oxygen gas giving/

giving P_4O . The mechanism then followed the course



* = excited molecule.

This gives P_4O_{10} as the final product and this was known to be the state of phosphorus pentoxide vapour.

If 1, 3, 4, 5 and 6 proceed wholly according to mechanism (a) one atom of oxygen gives rise to eleven new ones and a branching chain results. Deactivation of O atoms by recombination $O + O + X$ where X may be a gas molecule or the wall of the vessel breaks the chains. At the lower limit deactivation takes place at the walls and at the upper limit in the body of the gas. It can be shown that this scheme is energetically possible.

In 1929 Dalton and Hinshelwood¹⁷ produced a theory which does not depend on assumptions as to the nature of/

of the intermediates. They designated the chain propagators by X_O and X_P . X_O gives X_P on collision with a phosphorus molecule and X_P gives X_O on collision with an oxygen molecule. In this way the chain develops until either X_O or X_P is destroyed at the walls. From these assumptions they obtained Semenov's equation for the lower limit as follows.

Let $k_1 F(c)$ be the original rate of production of X_O .

Let $K [X_O]$ and $K [X_P]$ be the rates at which X_O and X_P are destroyed at the walls.

$$\text{Then } \frac{d[X_O]}{dt} = k_1 F(c) + \alpha k_2 [X_P][O_2] - k_3 [X_O][P_4] - K[X_O] = 0.$$

$$\text{and } \frac{d[X_P]}{dt} = k_3 [X_O][P_4] - k_2 [X_P][O_2] - K[X_P] = 0.$$

is introduced to take into account the branching of the chains. This gives

$$[X_O] = \frac{k_1 k_2 [O_2] F(c) + k_1 K F(c)}{(1-\alpha) k_2 k_3 [P_4][O_2] + k_2 K [O_2] + k_3 K [P_4] + K^2}$$

Assuming perfect efficiency for the $X_O + P_4$ and $X_P + O_2$ collisions $k_2 = k_3$, and since K is probably very small in comparison with $k_2 [O_2]$ and $k_3 [P_4]$ K^2 may be neglected. The condition for explosion is that $[X_O]$ should increase indefinitely and this is brought about if the denominator equals zero.

$$\text{i.e. if } (\alpha-1) k_3 [P_4][O_2] = K \{ [O_2] + [P_4] \}$$

Since K determines the rate at which X_O and X_P reach the walls it is inversely proportional to the total pressure.

i.e./

$$\text{i.e. } K = \frac{K'}{[O_2] + [P_4] + [X]}.$$

where $[X]$ is concentration of inert gas.

$$\text{Thus } (\alpha - 1)[P_4][O_2] = \frac{K'([O_2] + [P_4])}{[O_2] + [P_4] + [X]}.$$

and as concentrations are proportional to partial pressures

$$P_{P_4} \cdot P_{O_2} \left(1 + \frac{P_X}{P_{P_4} + P_{O_2}} \right) = \text{constant for a given tube.}$$

18

Melville and Ludlam carried out experimental work with numerous inert gases showing that in this equation p_X should be multiplied by a factor μ depending on the nature of the inert gas. μ was found to be inversely proportional to the diffusion coefficient of the inert gas. Examination of temperature coefficients gave additional evidence that μ probably depends on the diffusion of the chain carriers into the inert gas. King and Ludlam¹⁹ obtained still more evidence in support of this by comparative work with hydrogen, deuterium and helium as inert gases. As was to be expected deuterium and helium are very similar in their effects but hydrogen shows a value which is larger than that predicted by theory. King and Ludlam hold that this may be caused by inaccurate assumptions as to the nature and physical constants of the chain carriers.

If/

If deactivation at the upper limit is regarded as due to triple collisions with gas molecules similar equations are obtained, but no complete theoretical treatment of the upper limit has yet appeared. In general²⁰.

$$\text{Rate of reaction} = \frac{F(c)}{f_s + f_c + A(1-\alpha)}$$

Where $F(c)$ is a function of the concentration of reacting gases, f_s and f_c are coefficients to express the breaking of chains at surfaces and by triple collision in the gas, A is a constant generally large and α is a function for the branching of chains. f_s , f_c , and A all vary with the pressure of gas present. For a definite phosphorus pressure and very low oxygen pressure f_s is very large compared with f_c and the denominator is positive. For branching chains

$\alpha > 1$. As the oxygen pressure is increased f_s decreases much faster than f_c increases until at the lower limit the denominator is zero and explosion takes place. At still higher oxygen pressures f_s is negligible but f_c is increasing rapidly until at the upper limit the denominator ceases to be negligible and reaction becomes non-explosive.

Altering the rate of initiation of the chains alters the rate of the steady reactions. Where the reactions have been shown to be temperature dependent the position of the limits is very sensitive to changes/

21.22.23.24.
 changes in the rate of chain initiation. In these reactions the efficiency of the chain propagators is considerably less than 100%, and the deactivation efficiency of the walls may also be less than 100%. In the case of phosphine-oxygen and phosphorus-oxygen, both these effects are 100% efficient and the position of the limits is temperature independent. Change in rate of chain initiation should therefore not affect the position of the limits.

25.26.
 This was tested by Melville and Roxburgh^{25.26.} who used photochemical means to initiate the chains in the phosphine-oxygen reaction. They found that the lower limit was lowered and the upper limit raised. The method was to illuminate the gases at pressures at which no reaction took place and then change the oxygen pressure increasing it at the lower limit and decreasing it at the upper limit until explosion occurred. They found that at the lower limit the effect persisted for several minutes after illumination, but that at the upper limit no change in limit could be obtained two seconds after illumination. The change in the lower limit was explained by them as due to a change in the state of the wall of the vessel. A similar change in the lower limit of the phosphorus-oxygen reaction was obtained by King and Ludlam,¹⁹ who found that if the gaseous mixture was illuminated in one vessel and then transferred to an exactly/

exactly similar vessel no change in limit was obtained.

With regard to the upper limit for phosphine and oxygen, Melville and Roxburgh found that the change is very sensitive to small amounts of water vapour and that changes in temperature have a comparatively large effect. They suggested that the true upper limit is that observed on illumination, and that the one normally observed is too low since there are not enough chains being started for the upper limit relationship to hold. King and Lullam attempted to repeat these experiments with phosphorus and oxygen. They found a similar effect, but could not definitely confirm their results owing to the difficulty in obtaining a constant value for the upper explosion pressure, due no doubt to the sensitiveness of the reaction to traces of impurities.

This difficulty in obtaining strictly reproducible results is a common feature of upper limit work, and explains why so much has been done on the lower limit in comparison with what has been done at the upper limit. Some work has been done on rate of reaction above the upper limit, but again this is little in comparison with what has been done on reactions beneath the lower limit. In the paper mentioned above Melville and Roxburgh²⁵ showed that above the upper limit the length of the chains in the phosphine-oxygen reaction decreases steadily with increase in oxygen pressure. This is in accordance with theory, the increase in gas pressure increasing/

increasing the chance of chains being broken in the gas phase. They gave the following expression for the rate above the upper limit

$$\text{Mercury sensitised} \quad - \frac{d[\text{PH}_3]}{dt} = \text{constant} \frac{[\text{PH}_3]}{[\text{O}_2]^2} \text{Intensity.}$$

$$\text{Direct Photo-reaction} \quad - \frac{d[\text{PH}_3]}{dt} = \text{constant} \frac{[\text{PH}_3]^2}{[\text{O}_2]^2}$$

and were able to show that deactivation is caused by the reaction $\text{X}_0 + \text{X} + \text{X}$ where X is $\text{PH}_3 + \text{O}_2$ or any other molecule present in the gas mixture. They showed that it is probable that X_0 is an oxygen atom and that the branching process is the collision $\text{X}_p + \text{O}_2$ yielding two oxygen atoms.

In view of the difficulties experienced in research at and above the upper limit it is desirable to consider the possibility of work in solution. Here the solvent molecules are so numerous that practically every collision between solvate molecules must take place in presence of one or more solvent molecules. In other words conditions are analogous to those which exist at pressures considerably above the upper limit.

The earliest work in the field of chemical kinetics was carried out in solutions, and it was from such work that the elementary theory of mono-, bi-, and trimolecular reactions was developed. But progress was slowed up and attention was turned to gaseous/

gaseous reactions, especially when it became possible to interpret these in the light of the Kinetic Theory of Gases and energy of activation. The number of collisions between molecules could be calculated and remarkable success was experienced in applying this method. A new impetus was given to research on solutions when it was shown to be possible in certain cases to apply this theory to solutions without serious error. But remarkably little was done in the way of comparing reaction rates in solution and in the gaseous state.

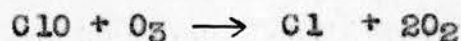
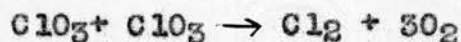
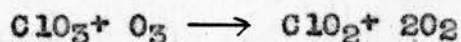
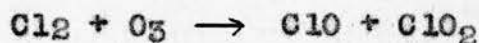
Among the reactions which were first subjected to a comparative study were the decomposition of ^{27.28.} nitrogen pentoxide and the isomerisation of ^{29.30.} pinene, both unimolecular and the more complicated decomposition of ^{31.32.33.} chlorine monoxide. All these proceed at similar speeds and in a similar manner in the gaseous state and in such solvents as carbon tetrachloride and chloroform for the first, petrolatum for the second, and carbon tetrachloride for the third. The last proceeds in consecutive stages. An interesting ^{34.35.36.} example is the decomposition of ozone. This may be bimolecular in the gas phase but in carbon tetrachloride solution the reaction is found to go at a greater rate and to be unimolecular. Examination shows that ozone has some action on the solvent but this/

this only occurs to a small extent. This may be the first stage of a chain or the reaction can be regarded as quasi-unimolecular in the gas phase with carbon tetrachloride acting as an 'inert gas' in the reaction in solution.

The catalysed decomposition of ozone has also been studied the catalyst being chlorine. In the gas reaction there is an initial induction period, followed by a faster reaction which proceeds according to the equation

$$-\frac{d[O_3]}{dt} = k[Cl_2]^{\frac{1}{2}}[O_3]^{\frac{3}{2}}$$

This expression is due to Bodenstein, Padel, and ³⁷Schumacher, who worked at temperatures of from 35°C. to 50°C where the uncatalysed reaction could be ignored. They give the mechanism



The induction period is regarded as the time required for ClO_2 and ClO_3 to attain stationary concentrations. From this scheme the required equation can be obtained. Bowen, Moelwyn - Hughes and/

and Hinshelwood³⁶ investigated the reaction in carbon tetrachloride solution. Here they had also to take the uncatalysed reaction into account. Assuming that these proceed simultaneously and independently. They obtained the expression

$$-\frac{d[O_3]}{dt} = \kappa [Cl_2]^{\frac{1}{2}} [O_3]^{\frac{3}{2}} + \kappa' [O_3]$$

and verified it experimentally.

Of late years it has been possible to do some comparative work on the reactions of organic compounds in the gaseous state and in solution. Among others, comparisons have been carried out with some polymerisation reactions³⁸ many of which rather surprisingly follow a simple kinetic course. Photochemical reactions have also been compared, and it has been found that quantum yields are often little different for reactions in the gaseous state and in solution in such solvents as carbon tetrachloride. For the decomposition of chlorine monoxide^{39,40.} and chlorine peroxide,^{41,42.} and the chlorine sensitised decomposition of ozone,^{43,36.} quantum yields of two have been obtained both in the gas and in carbon tetrachloride solution but for ozone higher yields are also obtained. Inert solvents such as carbon tetrachloride seem to have little effect on a reaction.

Carbon tetrachloride is regarded as an inert solvent since it is chemically saturated, unassociated, and/

and symmetrical (non-polar). Other solvents such as hexane and silicon tetrachloride may be expected to act similarly. Where it has not been possible to compare rates of reaction for gas and solution comparison with different solvents leads to similar conclusions. Menschutken⁴⁴ found that for the "slow" reaction between ethyl iodide and triethylamine the velocity of combination is slowest in hexane, $k = 4.92 \times 10^{-6}$, and fastest in benzyl alcohol, $k = 6.93 \times 10^{-3}$. On the contrary, hexane and carbon tetrachloride solutions give the fastest rates of reaction in the acetic anhydride - ethyl alcohol⁴⁵ reactions but such cases are few. Many attempts have been made to correlate properties of solvents with rates of reaction in solution, but it is often found that a classification which is suited to one reaction breaks down when it is applied to another reaction. One of the most useful classifications is that due to Richardson and Soper.⁴⁶ (1929). They hold that if the reaction products have higher cohesion, in other words greater internal pressure than the reactants, reaction will be favoured by solvents of high cohesion, and if the products have lower cohesion than the reactants reaction will be retarded by solvents of high cohesion. Other relationships used have been the dielectric constants and polarity of the solvents but since high dielectric constant/

constant, polarity and high internal pressure often run parallel similar results can be obtained using the different criterion. It must also be remembered that the occurrence of precipitation brings in solubility and may cause changes in rates of reaction where equilibrium exists among intermediates.

As is shown by the cases mentioned above some comparative work has been done on rates of reaction in the gas and in solution but the position is at present highly unsatisfactory. In many cases a reaction which is possible in solution may be very difficult to observe in the gaseous state due to such a factor as lack of vapour pressure of the reactants. In particular no reaction exhibiting explosion limits in the gaseous state has been studied in solution. Explosion limits in solution reactions would not be expected but points at which rapid change in reaction rate occurs have been found. The reactions phosphorus-oxygen and phosphine-oxygen would be very difficult to study in solution, since it has only been found possible to study them in the gas by pressure changes and the appearance of a flash on explosion. Bäckström⁷ used solutions of phosphorus in heptane but his method was to shake the solutions with gaseous oxygen and note the change in the volume of oxygen. Strictly speaking this is not a solution reaction at all.

It is therefore desirable to try to obtain data from/

from some reaction of a nature similar to the phosphorus oxidation. A likely set of reactions seemed to be those occurring between phosphorus and the halogens. No work had been done on these in the light of modern theory, in fact, apart from determination of the $\text{PCl}_3 + \text{Cl}_2 \rightleftharpoons \text{PCl}_5$ and $\text{PBr}_3 + \text{Br}_2 \rightleftharpoons \text{PBr}_5$ equilibria little work of any kind had been done in this field. As these reactions cannot proceed except in several steps it was thought likely that they might show explosion limits in the vapour state. Further the reactants are all soluble to some extent in ordinary solvents and a study of the reaction in solution seemed possible. Such a study would be equivalent to studying reactions at conditions similar to those above the upper limit if reaction in the gas phase should show explosion limits. The possibility of very complicated expressions being required had to be faced but it was also possible that reaction might take place according to simple relationships. It was therefore decided to investigate these reactions.

The reasons for doing so may be summarised:

(1) Unsatisfactory nature of knowledge with regard to upper limit.

(2) Solutions correspond to reactions considerably above the upper limit.

(3) Desirability of comparing reaction rates in gas and in solution.

(4)/

(4) Great difficulty would be experienced with $P_4 - O_2$ or $PH_3 - O_2$ in solution.

(5) Phosphorus and the halogens may be expected to react similarly to phosphorus and oxygen.

(6) No work has been done on phosphorus and halogens.

(7) It should be possible to study phosphorus - halogen reactions in gas and in solution.

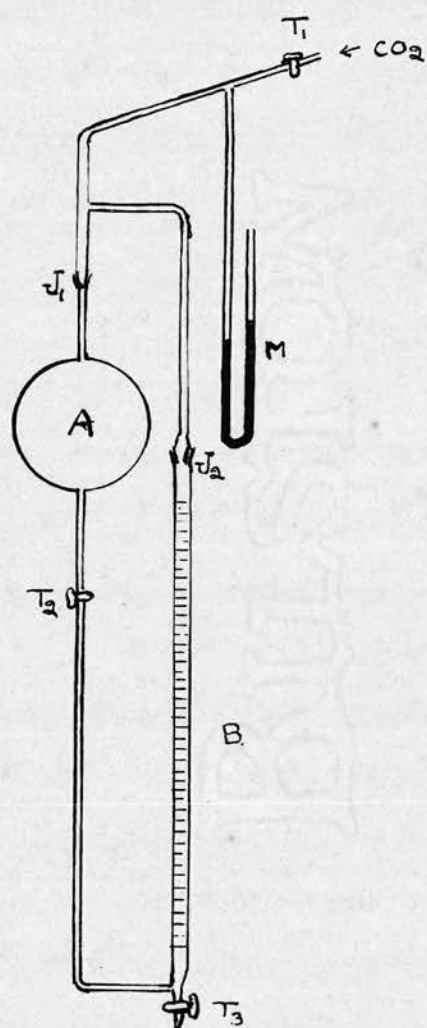


Figure II

T₁, T₂, and T₃ are taps.

M is a mercury manometer.

B is a burette.

The phosphorus solution was stored in A and could be run into B by opening T₂, the joining of A and B at the top allowing this to take place. T₃ made it possible for measured volumes of solution to be removed, the pressure inside the apparatus being kept just high enough to permit of this by periodically admitting carbon dioxide from a cylinder at T₁. M measures this pressure.

The apparatus was filled with phosphorus solution by lifting off the top at the ground glass joints and filtering the solution into A, which had previously been filled with carbon dioxide. The rest of the apparatus was then filled with carbon dioxide and the top replaced. In this way a pure solution was introduced into the container and since the only gas present was carbon dioxide no oxidation of the phosphorus took place. Since red phosphorus and oxides of phosphorus are insoluble in the solvents used (hexane and carbon tetrachloride) and had previously been removed by filtration, it could be assumed that all the phosphorus in the container was present as dissolved white phosphorus provided that no phosphorus came out of solution. If any phosphorus did come out of solution it was instantly detected as the samples withdrawn ceased to be clear and transparent, but generally/

generally this did not happen. To prevent formation of red phosphorus the apparatus was painted black except for the burette scale, which was guarded by a sheet of ebonite which could be turned round to the back of the burette when a reading was taken. All readings were taken in a red light as this does not encourage the transformation of white phosphorus into red phosphorus.

Determination of Phosphorus.

This presented much greater difficulty than had been anticipated. An attempt was made to titrate phosphorus by aqueous iodine using aqueous sodium thiosulphate and aqueous starch to determine the excess iodine, but this method was not feasible as iodine did not seem to oxidise phosphorus efficiently.

The following method was then tested.

The phosphorus solution was placed in a beaker under water and oxidised with liquid bromine. 3 to 4 cc. of 4 N NaOH were then added and after a short time 5 cc. conc HNO₃ and the solution boiled to remove excess bromine. A similar method was used by Miller⁴⁷ in her work on the phosphorus oxides. For determining the small quantities of phosphate produced by the oxidation it was decided to use the reduction of ammonium phospho-molybdate⁴⁸.

Reagents. A 5% ammonium molybdate in 5 N H₂SO₄

B 20% aq Na₂SO₃ crystals.

C 0.5% aq hydroquinone containing 1 cc.
N H₂SO₄ per 100 cc.

In qualitative analysis a drop of each reagent is added to 0.1 cc. of the solution suspected to contain phosphate, a positive reaction being indicated by a blue colour, which attains maximum intensity in half an hour and remains permanent for a considerable time. In quantitative work a known volume of unknown is taken, 4 cc. of A, 2 cc. of B and 2 cc. of C added. The solution is then diluted to a convenient volume (in this case 50 cc.) and after half an hour the colour is matched against a standard prepared in the same way. Under these conditions 0.01 mg. phosphate may be detected easily. The colour is due to the formation of a complex phospho-molybdate of unknown composition ~~and~~ which gives a deep blue on reduction with hydroquinone. Sulphuric acid is used to stabilise the reagents while sodium sulphite is used to destroy oxidising agents and enable the hydroquinone reduction to take place. Nitric acid might affect the reduction but in the quantities in which it was used and the amounts of sodium hydroxide and sodium sulphite present it was considered that this would be negligible.

To test the method 0.362 gm. white phosphorus was weighed out. This was done by cleaning the phosphorus with moderately concentrated nitric acid washing it with water and then drying it carefully with filter paper. It was weighed under water in a weighing/

weighing bottle. The phosphorus was then washed with water into a 250 cc. pyrex beaker and liquid bromine cautiously added. Oxidation proved so vigorous that it was necessary to add 10 to 15 ccs. carbon disulphide to dissolve the phosphorus and after this the reaction proceeded smoothly. 3 to 4 cc. 4 N NaOH were then added followed in a few minutes by 5 cc. conc. HNO₃ and the solution boiled over a small flame until all carbon disulphide and excess bromine were gone. The solution was now suitably diluted and the concentration of phosphate found by comparison with a standard solution of potassium hydrogen phosphate using the method described above. A Klett colorimeter was used. The results obtained were concordant to 2% but gave as originally present only 0.153 gm. phosphorus.

The process was repeated, the solution being thoroughly stirred at intervals during the oxidation but although 0.0094 gm. phosphorus was weighed out only 0.0019 gm. was found on analysis.

The next attempt was made using 0.191 gm. phosphorus and stirring the solution in the cold for 15 mins., then heating it to 35°C. and adding the alkali. After 10 mins. the acid was added and the solution heated on a waterbath the last traces of bromine being removed by boiling the solution. Only 0.183 gm. phosphorus was found. The process was repeated using 0.071 gm. phosphorus but only 0.050 was found on analysis. Glass rods to aid the evaporation did not have/

have any good effect nor did the addition of sodium peroxide in place of 4 N NaOH, results always being 10 to 50% low.

The error might possibly be due to the action of nitrate on the hydroquinone reduction. To test this 25 ccs. of a standard KH_2PO_4 solution containing 0.89 gm. phosphorus per litre were taken and 20 ccs. hexane added. 5 ccs. liquid bromine were added followed in a few minutes by 3 to 4 cc. 4N NaOH and the solution warmed gently. After 10 mins. 5 cc. conc. HNO_3 were added and the hexane and excess bromine removed by heating the beaker over a small flame. On determination of the phosphorus it was found that apparently the original solution contained only 0.81 gm. phosphorus per litre. Repetition of the colorimetric determination gave the same result and when the process was repeated with a fresh sample and more cautious evaporation of the liquids the value obtained was 0.84.

As difficulty was experienced in removing the last traces of bromine without vigorous boiling it was thought that perhaps phosphate was being removed in some way in this process. Also where such solvents as carbon disulphide are present the carbon disulphide is the bottom layer and there is a tendency for bumping to take place. Use of a separating funnel might remove some organic liquids but it would not solve the problem/

problem of removing bromine. The following method was therefore tried.

25 cc. standard KH_2PO_4 were taken and 20 cc. hexane and 20 cc. liquid bromide added. This was warmed gently on a sandbath to 30°C . and the NaOH added as usual followed in 10 mins. by the usual HNO_3 . A stream of air was now passed through the solution and when the temperature had reached 80°C . all the bromine and hexane was gone. The process took about 45 mins. When the phosphorus content was determined in the usual manner the standard was found to contain 0.88 gm. phosphorus per litre. This is satisfactory especially when it is remembered that the amount of bromine added is far in excess of anything likely to be necessary in practice. Repetition with as organic liquids 5 ccs. carbon disulphide, 8 ccs. benzene, 12 ccs. carbon tetrachloride and 20 cc. hexane present simultaneously and also 15 ccs. liquid bromine gave the same result. Apparently the errors were not due to the presence of nitrate but to the methods used to remove bromine and organic liquids.

The following results were obtained using this method of heating and with CCl_4 present to dissolve the phosphorus. This solvent was going to be used in subsequent work.

TABLE 1./

TABLE 1.

<u>Weight of Phosphorus.</u>	<u>Weight of Analysis.</u>	<u>Error.</u>
0.209 gm.	0.208 gm.	- 0.5%
0.104	0.105	+ 1.0%
0.166	0.167	+ 0.6%
0.261	0.260	- 0.4%
0.176	0.175	- 0.6%
0.214	0.203	- 5.5%

The last value is low but the rest are as good as can be expected from a colorimetric method. Two colorimetric determinations were made in each case. Using this method in subsequent work no difficulty was experienced. Oxidation and the removal of the organic liquids takes about one hour and one hour was given to develop the colour. The whole operation can be carried out in under three hours and it is possible to have several going at once.

PHOSPHORUS AND IODINE IN SOLUTION.

It is first necessary to discuss the numerous iodides of phosphorus which have been reported. Owing to the tendency for red phosphorus to be formed, great diversity of opinion has been expressed as to the iodides which are formed.

The diiodide, P_2I_4 , and the triiodide, PI_3 , have been prepared and their melting points, vapour densities, and properties determined, but the existence of the penta iodide has never been proved though it has been claimed by Hampton.⁴⁹ The diiodide is usually prepared by mixing phosphorus and iodine in equivalent proportions in carbon disulphide and cooling to $0^\circ C$. The crystals then separate out and the solvent can be removed in a current of dry air. These are pale orange in colour and decompose slowly in presence of moist air. The melting point of P_2I_4 was given as $124.5^\circ C$ by Traxler and Germann.⁵⁰ The triiodide can be prepared by the same method using equivalent proportions of the elements. It crystallises as red plates and decomposes more readily than the diiodide.

Other iodides which have been claimed are the tetrata iodide P_4I and the tritattetraiodide P_3I_4 .

P_4I was claimed by Boulouch⁵¹ who added dry iodine to a solution of phosphorus in carbon disulphide in quantity less than is necessary to produce the diiodide/

diliodide and exposed the mixture to sunlight. He obtained an amorphous red powder which he reported as a definite iodide P_4I , but Siemens⁵² considers that he only obtained the diliodide contaminated with red phosphorus. No melting point has been obtained for P_4I , and on heating, P_2I_4 and phosphorus vapour were obtained. Also, sunlight promotes the transformation of white to red phosphorus, and iodine in small amounts is known to catalyse the change being used commercially for this purpose. Further all the reactions claimed by Boulouch for P_4I can be obtained with a P_2I_4 red phosphorus mixture so it is practically certain that Siemens is correct in his criticism.

Besson⁵³ assumed P_3I_4 to be present as an intermediate in the catalytic white phosphorus - red phosphorus change where solutions in carbon tetrachloride are used with iodine as catalysts. He obtained red phosphorus followed by P_2I_4 and analysed his solutions before and after the removal of these. He claimed that the phosphorus and iodine were used up in a ratio corresponding to P_3I_4 and on this evidence alone suggested that P_3I_4 was present in solution.

He assumed $P_3I_4 + \text{light} \rightarrow P_2I_4 + \text{red P.}$

It is of interest to note that his reactions took several days but his method cannot be said to give evidence for the existence of P_3I_4 .

In view of the above it may be said that phosphorus/

phorus and iodine react to give the diiodide in solution if the iodine is present in the required proportions or less. Under suitable conditions red phosphorus is produced. If the amount of iodine present is greater than what is required to give the diiodide the triiodide is produced. By working with solution containing as a maximum as many iodine equivalents as phosphorus equivalents, phosphorus diiodide should be the only iodide obtained and red phosphorus may also appear under suitable conditions.

Extent of Dissociation of Phosphorus Diiodide.

2 gms. P_2I_4 were prepared according to the method of Traxler and Germann. (method given above). Orange red crystals M.P. = 120° were obtained but they tended to decompose before melting, and after they had been kept for one week in a desiccator some decomposition had taken place with production of red phosphorus and probably also acids. Fresh P_2I_4 was prepared and when a sample was shaken with aqueous starch no blue colour was obtained. The next day a sample was taken and shaken for several minutes with hexane and when aqueous starch was shaken with the solvent a pale blue colour was seen. On repeating the process with carbon disulphide, carbon tetrachloride and cyclohexane as solvents no blue colour was obtained but with benzene the blue colour again appeared. This indicated the presence of iodine in these solvents at or about the/

leave 3
lines blank
(inches)

the limit at which the blue complex is formed with starch. It was necessary to decide whether dissociation of the diiodide takes place in all solvents or slight dissociation occurs in hexane and benzene and none in the other solvents used. Mylius⁵⁴ says that the limit at which the blue can be seen in water is the presence of 10^{-4} gm iodine per litre but little guide to the limit at which it is seen with other solvents exists. The partition of iodine between starch and organic solvents has been investigated e.g. by Murray⁵⁵ for carbon tetrachloride, but this work has been carried out in order to establish if possible the nature of the complex rather than to determine the exact degree of sensitiveness of the reaction. This last will depend on the conditions of experiment and the method used to prepare the starch solution.

It was decided to test the relative effect of different solvents on the blue complex. The starch solution was the same as had previously been used and was prepared by mixing 1 gm. soluble starch with a little cold water, adding this to 200 cc almost boiling water and boiling for one minute. When the solution had cooled 5 cc dil HCl were added as preservative. The method used was to shake 5 cc of aqueous starch with one or two drops of aqueous iodine and then add 5 cc. of solvent and shake up the mixture. The colour was compared with that given by a standard in /

in which 5 cc of water formed the added solvent. The concentrations given are referred to the original 5 cc starch. Where the liquids are miscible the final concentration of iodine will be half this and where they are not it will depend on the partition coefficient.

TABLE 2.

<u>Solvent</u>	<u>Effect</u>
Water	Pale blue with 0.002 gms iodine/ litre
Carbon Tetrachloride	} Similar to water
Benzene	
Hexane	
Cyclohexane	
Chloroform	
Carbon disulphide	$I_2 = 0.004$ gm./litre. Mauve colour of same intensity.
Toluene	Blue fading in 1 sec. 0.025 gm I_2 /litre. Fairly permanent blue.

Solvents such as alcohol, methyl alcohol, acetone and ether all coagulated the starch and gave brown colour at much higher iodine concentration.

In view of the above the concentration of iodine in the solvents must be less than 0.002 gm I_2 /litre. The solubility of P_2I_4 in the solvents tried is small but considerably larger than this. Also there is the possibility that slight decomposition of the P_2I_4 occurred overnight to give traces of free iodine.
In /

In later work concentration of phosphorus was much higher than that necessary to take all the iodine to the diiodide, and where aqueous starch was added on the completion of reaction no blue colour was ever obtained, so phosphorus diiodide may be regarded as undissociated under the condition of experiment.

METHODS OF FOLLOWING REACTIONS.

The methods used to prepare, determine and store phosphorus solutions have already been given. Iodine solutions could easily be prepared and were determined by shaking samples with aq. $\text{Na}_2\text{S}_2\text{O}_3$ adding water to increase the aqueous layer and removing the organic liquid with a separating funnel. Excess thiosulphate was then determined with aqueous iodine using aqueous starch as indicator. Small amounts of the organic solvent (carbon tetrachloride or hexane) did not affect the end point. The initial iodine and phosphorus concentrations were obtained from the concentrations of the stock solutions and the relative volumes used.

Any method of following the course of the reaction must be such that it either has no effect on the course of the reaction or stops the reaction completely at some point and allows of analysis of the system. An attempt was made to follow the reaction by means of a green-sensitive photocell, a sensitive galvanometer, and a light source of weak intensity. By this means it was hoped to observe the fall in the iodine concentration /

*at present
omit all
fill p59*

centration without promoting photochemical reaction. Unfortunately the method was rendered inapplicable by the extreme sensitiveness of the system to light and the amount of scattering taking place. This light effect which extended throughout the visible spectrum ruled out the use of colorimetric methods unless samples were taken and hastily examined. The error here would be fairly large. Physical properties such as density of solution gave no assistance.

At this stage it was decided to see what could be done by analytical methods. This entailed stopping the reaction in such a way that the concentrations of at least one and probably all of phosphorus, iodine, and iodide at that point in time could be determined. The difficulties in doing so were found to be unexpectedly great and finally they proved unsurmountable. It was finally necessary to proceed by taking samples and hastily estimating their iodine content by visual comparison with standards, but before this was done a thorough examination of all possible analytical methods had been made.

APPLICATION OF PHOTOCELL.

The apparatus is shown in Figure III.

The reaction vessel was a glass cell 1.5 cms x 11 cms which was placed in a glass thermostat. The cell was so arranged that it could easily be removed and returned again to the exact position it had previously /

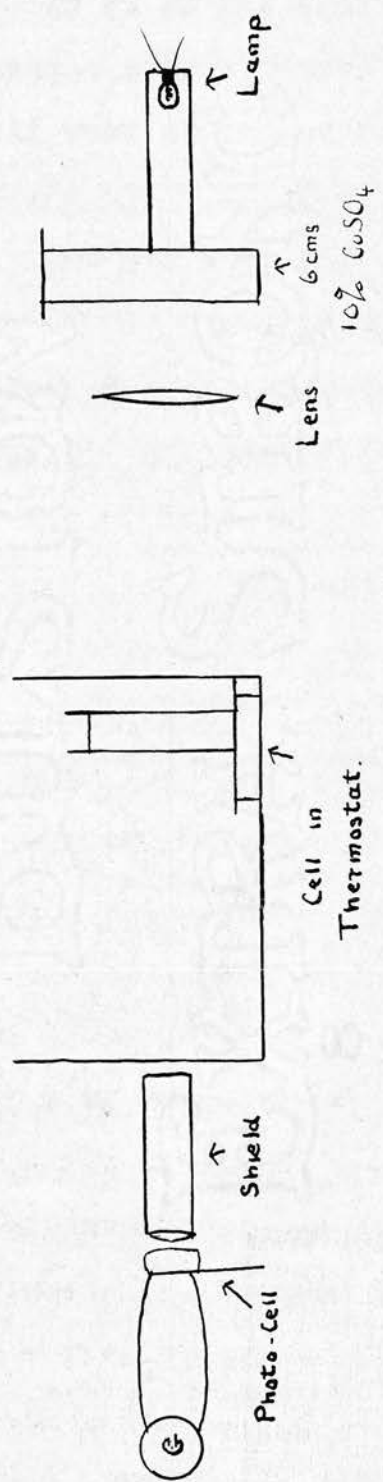


Figure III

viously occupied. The top could be closed by a microscope slide. The thermostat was electrically controlled and maintained at 25°C. A glass thermostat was used in preference to a copper one with glass windows, since copper is very liable to cause fungoid growth which hinders the passage of light. A further precaution was the addition of a little mercuric chloride to the water.

The light source was a 6 volt bulb run from three large 2 volt accumulators. These showed a very slight voltage drop as time went on but this was counteracted by inserting a variable resistance in the circuit and adjusting for constant light intensity.

The copper sulphate solution allowed mainly green light to pass, and this was focussed by the lens so as to pass through the reaction vessel and be picked up by the photo-cell. This was a green sensitive Westinghouse photronic cell and was shielded so that only the beam coming from the lens could reach it. The current produced was measured by a sensitive galvanometer. The only other light which was allowed to fall on the reaction vessel was an intermittent red light from the carbon heating lamp in the thermostat. This was not picked up by the photocell and was not expected to influence the rate of reaction. As the green light used was feeble it was not expected to influence the reaction either.

The reaction vessel was filled with carbon dioxide,
and /

and after a known volume of phosphorus solution had been introduced from the phosphorus container it was placed in the thermostat and allowed to attain constant temperature. Iodine solution was then added from a pipette which delivered its contents in one second. A stop-clock was started half a second after delivery from this pipette had started, and this was taken as the starting point of the reaction. The sudden inrush of iodine solution was found to cause complete mixing to take place almost instantaneously.

Hexane and carbon tetrachloride have been mentioned in the introduction as inert solvents. It was decided to use hexane which has been in favour lately as an ideal solvent. Phosphorus has no effect on it and in the absence of strong light iodination does not occur.

At first the following method was used. The reaction vessel containing phosphorus solution was placed in the thermostat and once constant temperature had been established (20 mins. were allowed) the resistance in the lamp circuit was adjusted until the galvanometer gave a constant deflection, exactly the same value being used for each experiment. No difference in deflection was found when the cell contained phosphorus solution and when it contained pure hexane. Iodine solution was then added in the manner mentioned.

The behaviour of the galvanometer is shown in Figure IV.

A gives the deflection before addition of iodine.

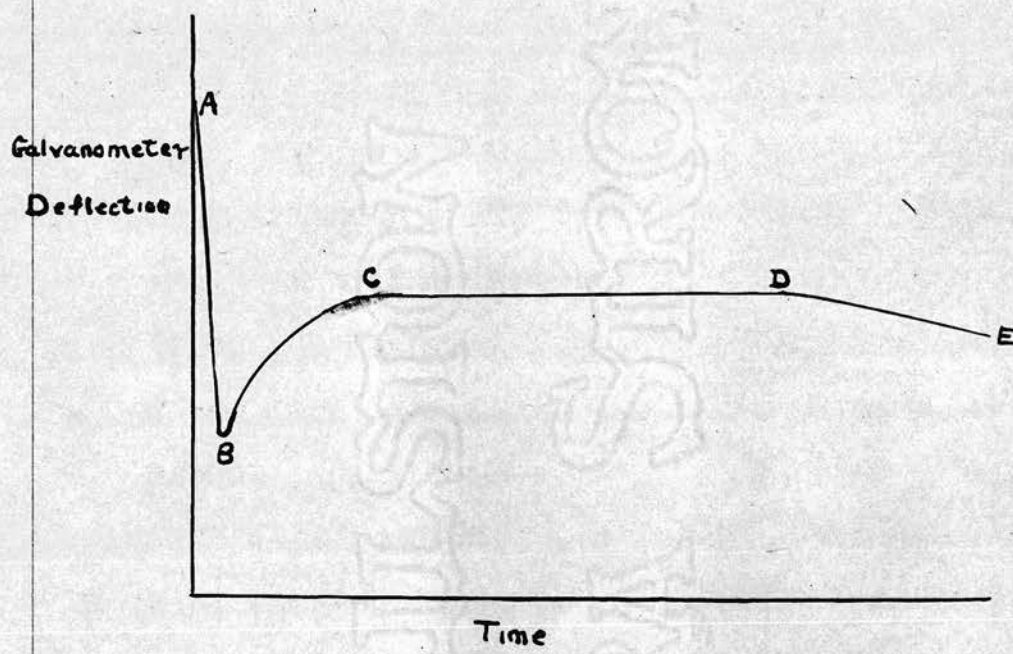


Figure IV

When iodine is added a fall takes place along AB at a rate which depends on the time of swing of the galvanometer. At B the deflection corresponds to the concentration of iodine present in solution and the rise along BC is due to the removal of iodine as reaction proceeds.

It is to be noted that constant deflection as shown by CD is less than for pure phosphorus solution. This was at first thought to be due to absorption due to iodides in solution but closer examination showed that much scattering of light was taking place. When the cell was left for several minutes (from A → C was only a matter of 1 or 2 minutes) the portion of the curve given by DE was obtained. This was accompanied by the coming out of solution of a reddish yellow suspension which was found to settle out overnight and to be insoluble in water. Hence it could not be an iodide or oxide of phosphorus and ^{must} be red phosphorus. The question now arose as to whether at C there was any equilibrium between the products and reactants. On careful examination it was seen that no iodine colour remained at this point and addition of aqueous starch gave no blue colour. Hence complete reaction had taken place.

In these experiments the concentration of phosphorus was $0.003 \rightarrow 0.001$ moles P_4 /litre and of iodine $0.001 \rightarrow 0.0005$ moles I_2 /litre the iodine concentration always being the smaller. In hexane iodine /

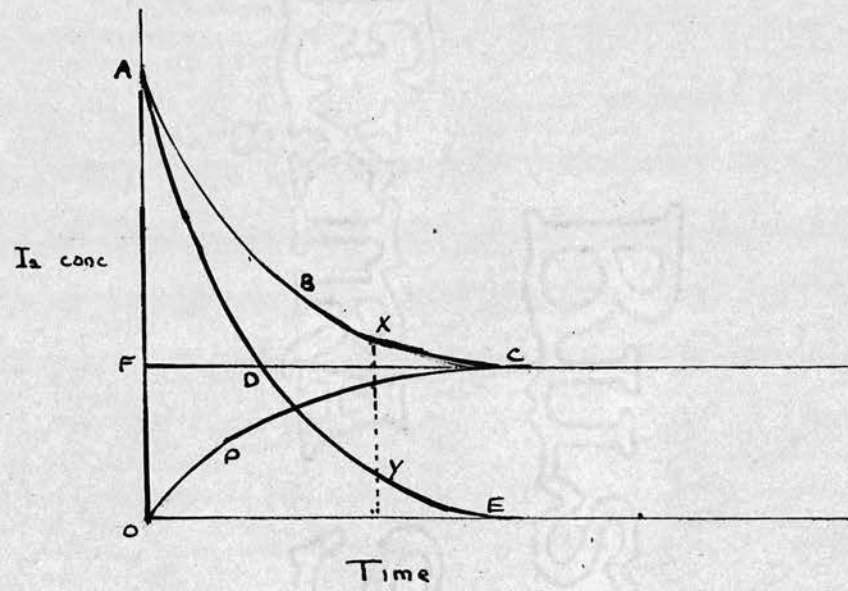


Figure V

iodine exists as I_2 molecules and phosphorus is generally regarded as being P_4 in solution. For P_2I_4 to be formed 1 molecule P_4 takes up 4 I_2 molecules hence these concentrations give ample phosphorus for all the iodine to be converted to the diiodide.

One of the difficulties encountered was that the galvanometer had a time lag of 15 to 20 seconds. Another galvanometer with a time lag of only 5 seconds was used in place of it and the small loss in sensitivity was more than compensated for by the possibility of following the reaction during most of its course. The reactions were then proceeded with as before. The time required for the galvanometer reading to fall to a value corresponding to the iodine concentration was only a few seconds and after this the deflections were noted and also the corresponding times the reactions had been proceeding. The corresponding iodine concentrations were read off a calibration curve and plotted against time. This is given by ABC in Figure V. A is the initial iodine concentration and the line FDC represents the constant value given by CD in Figure IV. Actually no iodine was left at this point and the apparent iodine concentration is due to scattering and absorption due to iodides.

If the actual iodine concentration is given by ADE, and OPC represents the amount of iodine which would give a loss of light equal to that taking place due to scattering, then any point on ABC is obtained from the sum of the corresponding points of ADE AND

OPC. Also it is reasonable to assume that OPC and ADE are similar curves and hence ABC will be similar to ADE and OPC.

Now if AO = a and FO = c, and X and Y are corresponding points on ABC and ADE giving iodine concentration x and y it can be shown that

$$\frac{y}{x - c} = \frac{a}{a - c}$$

True I ₂ conc.		Initial I ₂ conc.	
Apparent I ₂	- App final I ₂ conc	Initial I ₂	- App final I ₂ conc.

Since all the values are known except y the curve ADE can be calculated from the curve ABC.

As a working hypothesis it was assumed that the determining factor is the rate at which P₄ and I₂ collide and the probability of their reacting. It was assumed that reaction goes straight to P₂ I₄ as soon as the initial reaction takes place and that no noticeable concentration of intermediates is set up.

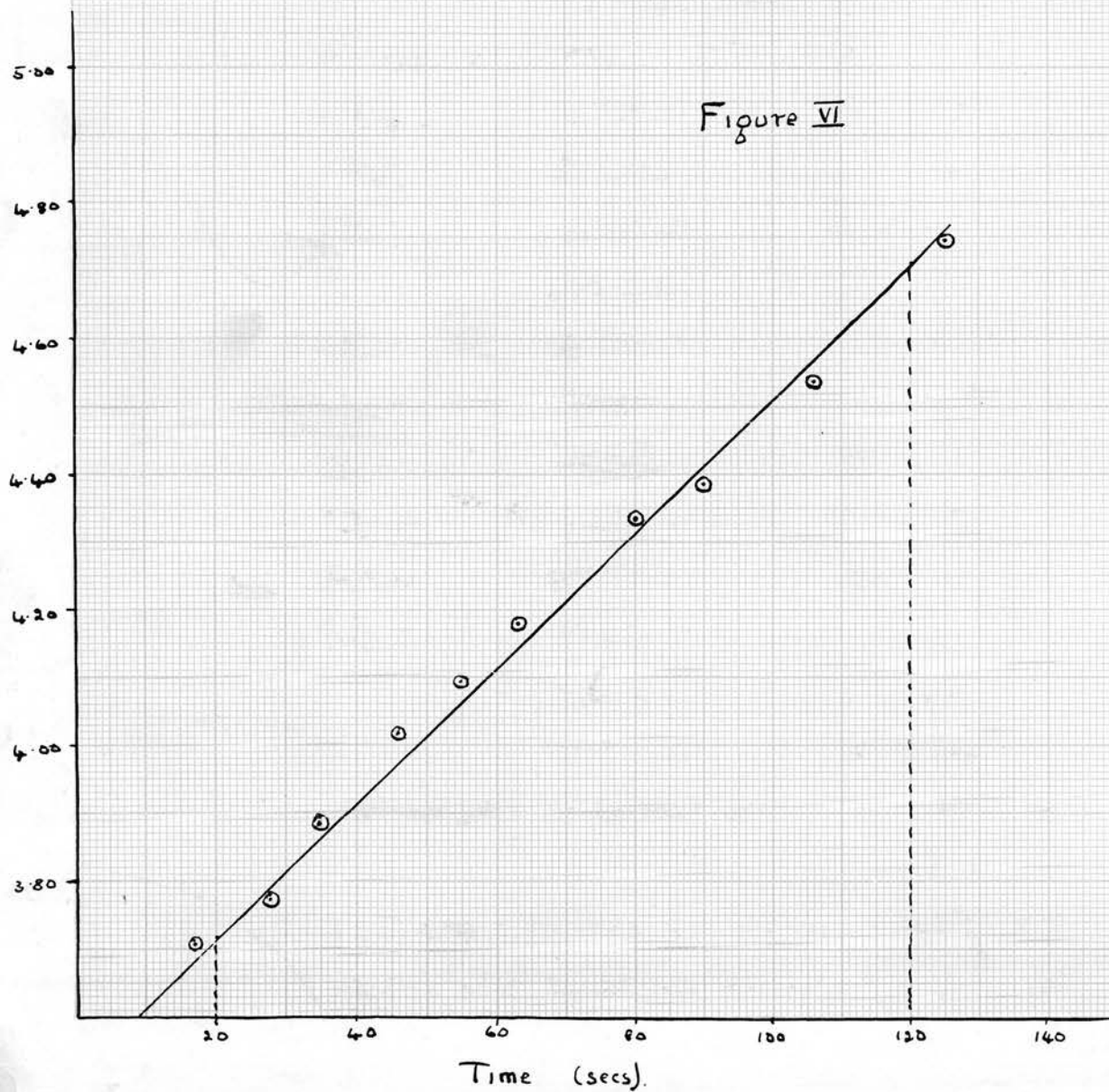
$$\text{Thus Rate} = k [P_4][I_2]$$

Since $\frac{1}{\text{mole}} P_4$ requires $\frac{4}{\text{moles}} I_2$ to give 2 moles P₂ I₄, (a - x), (b - 4x) and 2x are the number of moles per litre of P₄, I₂ and P₂ I₄ at a given time where initial P₄ and I₂ concs are a and b moles P₄ and I₂/litre.

Hence on the above assumption.

$$\text{Rate of reaction} = \frac{dx}{dt} = k(a-x)(b-4x)$$

which gives $t = \frac{1}{k(b-4a)} \log \frac{a(b-4x)^4}{b^4(a-x)}$

$\text{Log } \frac{1}{b-Lx}$ 

With the proportion of P_4 and I_2 being used the change in P_4 conc is in $(a - x)$ can be ignored and

$$t_2 - t_1 = \frac{1}{k(4a - b)} 4 \log \frac{(b - 4x_1)}{(b - 4x_2)}$$

whence k may be obtained by plotting t against $\log \frac{1}{b - 4x}$ and applying the above relation.

Seven cases were examined, a typical one being given.

$$a = 0.0078$$

$$b = 0.000230$$

Table 3.

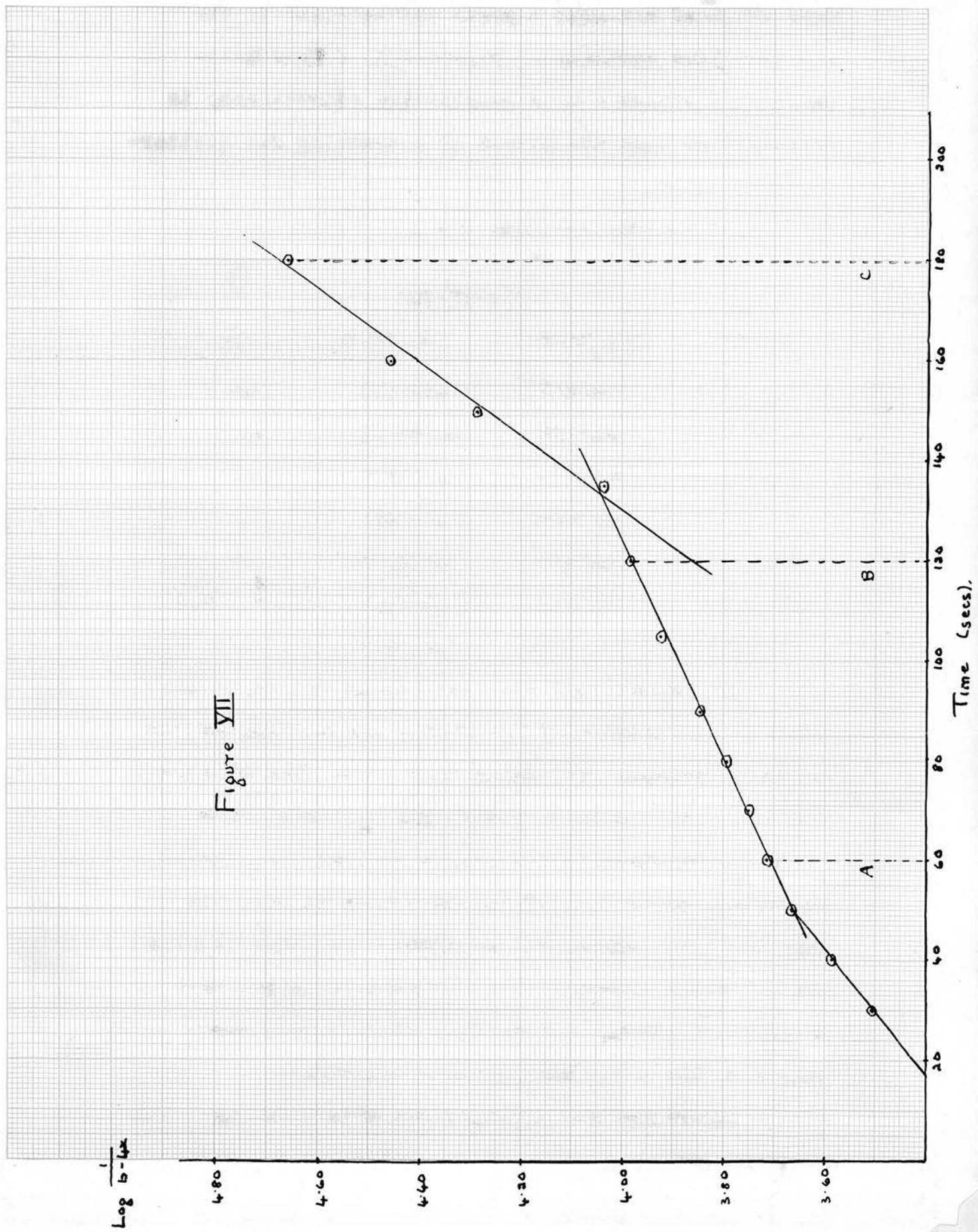
T (secs)	$(b-4x)$ apparent	$(b-4x)$ corrected	$\log \frac{1}{b-4x}$
17	0.000203	0.000197	3.706
28	0.000179	0.000168	3.775
35	0.000148	0.000130	3.886
46	0.000120	0.000096	4.078
55	0.000107	0.000080	4.096
63	0.000097	0.000068	4.180
80	0.000079	0.000046	4.337
90	0.000045	0.000041	4.387
106	0.000065	0.000029	4.538
125	0.000056	0.000018	4.745
150	0.000045	0.000005	
Final	0.000041	0.000000	

This gives a straight line graph (Figure VI.) and hence $k = 2.9$.

The volume of liquid in this case was 71.6 ccs.

In six of the cases graphs of this nature were /

Figure VII



were obtained but once a graph corresponded to two straight line portions. Figure VII. This indicated that either a more complicated relationship is necessary or that the method of correcting for scattering is invalid.

The results obtained are :-

Table 4.

<u>Volume</u>	<u>P₄ conc.</u>	<u>I₂ conc.</u>	<u>I₂</u>
71.6 ccs	0.0078	0.000230	2.9
95.4	0.0055	0.000173	8.5
79.4	0.0096	0.000207	6.0
91.9	0.0048	0.000299	5.1
88.7	0.0041	0.000309	11.0
86.4	0.0036	0.000318	A → B 2.9 B → C 8.8
105.8	0.00162	0.000259	21.6

The values of k show very large variation and could not be improved by including expression for the volume of solution or the surface area. Use of other than the first power of the P₄ and I₂ concs. made little improvement. The hexane used was the purest obtainable and all solutions were made up from the same stock of hexane, but no steps were taken to have the solvent absolutely dry. Phosphorus might tend to be oxidised during the reaction if moisture were present and this would have some drying effect.

It was decided to study the effect of light on the reaction.

EFFECT OF LIGHT, TEMPERATURE, SURFACE AND MOISTURE.

A study of these effects was made by mixing phosphorus and iodine solutions and leaving one portion in the dark while another portion in a similar test-tube was treated in various ways. The results obtained may be summarised.

1. Iodine was used up much quicker in pale green light than in the dark.
2. Iodine was used up much quicker in red light than in the dark and also faster than in green light, but the red light used was much more powerful than the green light.
3. Testtubes were placed in a large volume of water at the same temperature and the red and green lights still caused an increase in reaction rate. Hence this is not a temperature effect.
4. Two samples were left in the dark, one at 50°C and the other at 15°C . The one at 50°C reacted only about 20% faster than the other.
5. Moisture increases the rate of reactions several times.
6. When glass beads were present in one of two samples in the dark, no difference in reaction rate was noted unless the test-tube with the glass beads was vigorously shaken. The difference here might well be caused by local frictional heating. It was only a small difference. Hence surface effect if any is small.
7. /

46(a)



492 μ

546 μ 549 μ 549 μ

Figure VIII

7. Red phosphorus was usually deposited by the solutions exposed to light but it was very seldom obtained in the dark reaction.

8. When the phosphorus concentration was high enough to take all the iodine to the diiodide complete reaction always took place, although when the concentration was near the exact values required reaction sometimes took several days.

This reduces the value of the work done by the photocell method since the solutions were not thoroughly dried and the beam of green light and the intermittent light from the carbon heating lamp both affect the reaction rate.

ABSORPTION OF PHOSPHORUS DIIODIDE.

Some absorption photographs were obtained using a two prism glass spectrograph pointlight lamp and lens. These are shown in Figure VIII..

1. Initial iodine concentration = 0.00023 moles I_2 /litre.

Initial phosphorus concentration = 0.0072 moles P_4 / litre.

This solution had been allowed to react in presence of light and had then been left overnight in the dark until all the red phosphorus had settled out and solution had become clear.

2. Hexane.

3. /

3. Iodine was added to 2 until $I_2 = 0.00032$.
4. Phosphorus added until $I_2 = 0.00027$ and $P_4 = 0.0037$. solution allowed to react in presence of strong light and photographed while much scattering was still taking place.
5. Lamp.
6. Mercury vapour lamp.

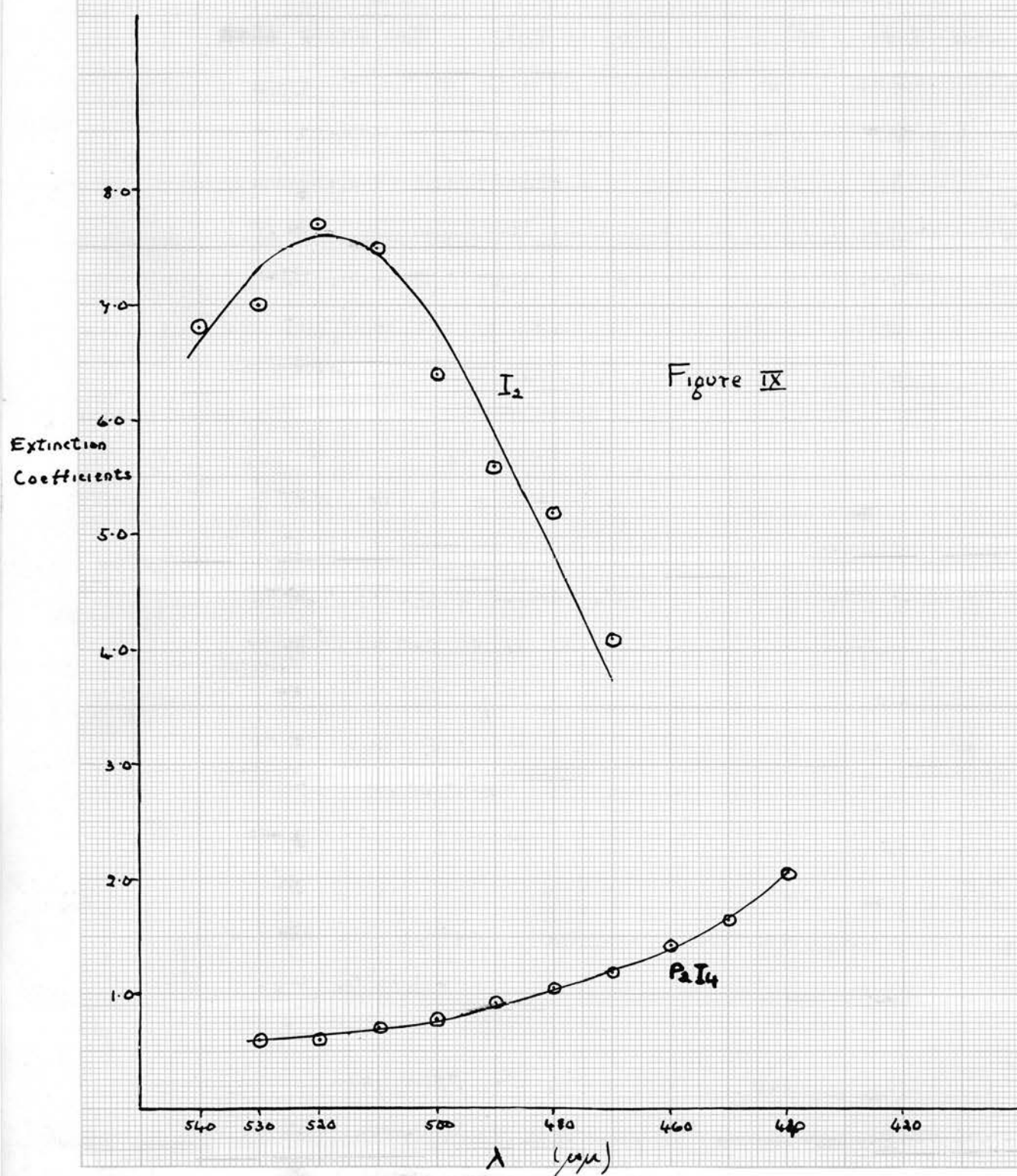
Exposure in 1. 5. was 10 secs in 6 1 second.

There is little difference between 2 and 5. No. 3 shows strong absorption in the green due to iodine but no absorption in the green is to be seen in either 1. or 4 although in 4. there is much diminution in light intensity in the blue probably due to light scattering. A very little loss of light in the blue is to be seen in 1. and this is probably genuine absorption by iodide.

A Hilger-Nutting Wavelength Spectro (photometer was made use of to obtain a more accurate indication of the absorption of P_2I_4 . With this instrument it is possible to determine the absorption taking place at any wave-length of the visual spectrum. The solvent used in this case was carbon tetrachloride as it had been decided for reasons to be described later to use this solvent for future work.

The concentration of the iodine solution used as standard was 0.00091 moles I_2 /litre.

The /



The P_2I_4 solution was obtained by allowing P_4 and I_2 to react in the dark thus obtaining a clear P_2I_4 solution. This contained 0.0052 moles P_2I_4 /litre assuming all iodine had gone to P_2I_4 . The extinction coefficients referred to 0.01 mole I_2 or P_2I_4 /litre are shown in Figure IX. The values are comparative not absolute, and show that the absorption of P_2I_4 in the green and even some way into the blue, is so much less than that of iodine that it may be ignored, when the colour of iodine is being used to indicate the concentration of iodine in solution.

ANALYTICAL METHODS.

It was now decided to investigate the possibility of using some analytical method to follow the course of the reaction. The simplest method seemed to be to shake the solution with water and determine the iodide in solution, but this could not be done unless some method was used to remove phosphorus or iodine and thus stop the reaction instantaneously. Thiosulphate was immediately thought of as likely to take out all the iodine, but the probability of reaction between the free phosphorus present and the thiosulphate made it desirable to try other methods first.

One suggestion was that a dry free metal might take iodine out of solution in organic solvents and leave phosphorus and iodides unaffected.

Zinc /

Zinc dust, mercury, and silver foil were tried but any reaction which did take place was much too slow. Organic substances having an affinity for iodine were reviewed but none capable of reacting with the necessary speed could be thought off. Aqueous CuSO_4 and AgNO_3 are known to react with free phosphorus but they also react with iodine, and with the acids of phosphorus and the hydriodic acid produced by hydrolysis of phosphorus iodides, so they could not be used.

The next possibility was that a phosphite solution might be used to pick up free iodine and that the excess phosphite could be titrated with iodine. All the free phosphorus would remain in the organic liquid and this could be separated off before titrating the excess phosphite. Possible difficulties lay in obtaining a pure phosphite solution and in allowing for lower acids of phosphorus produced in the hydrolysis of the iodides. An approximately 0.2% solution of Na_3PO_3 was made up and shaken with iodine in hexane but little change in the concentration was observed. Alkaline solutions removed the iodine but on their being acidified iodine reappeared. Thus the reaction of phosphite and iodine is much too slow to be of service.

It is known that the oxidation of phosphorous acid by iodine is reversible. If alkali is present to remove acid produced reaction proceeds fairly rapidly but in presence of dilute acids little or no reaction /

reaction takes place. A portion of the above sodium phosphite solution was left overnight in presence of a little dilute hydrochloric acid after enough aqueous iodine had been added to colour the solution slightly, and next morning it was found that there had been no change in the iodine colour. In view of the fact that the halogens have little action on hypophosphoric acid in the cold a possible method of analysis suggested itself. This was to use slightly acid $\text{Na}_2\text{S}_2\text{O}_3$ to remove iodine from the reaction. This process should take place instantaneously and also all iodides would be hydrolysed to give HI , H_3PO_3 , and H_3PO_2 . Free phosphorus was not expected to have any great effect on thiosulphate and could be removed by separating off the organic liquid. An aqueous solution containing HI , H_3PO_3 , H_3PO_2 , $\text{Na}_2\text{S}_2\text{O}_3$ and $\text{Na}_2\text{S}_4\text{O}_6$ would be left, and provided the solution was kept slightly acid, it should be possible to titrate the thiosulphate with aqueous iodine. Hence the amount of free iodine in the organic liquid when $\text{Na}_2\text{S}_2\text{O}_3$ was added could be determined.

A 0.01003 N $\text{Na}_2\text{S}_2\text{O}_3$ solution was prepared and also an aqueous iodine solution, one cubic centimetre of which was found to be equivalent to 0.741 cc $\text{Na}_2\text{S}_2\text{O}_3$. 10.00 cc $\text{Na}_2\text{S}_2\text{O}_3$ were taken and 20 cc of the Na_3PO_3 solution mentioned above and 5 cc dil. HCl added, the whole diluted to 100 ccs, and titrated /

titrated with iodine using aqueous starch as indicator. The error was +0.2%. This was repeated, only this time about half the required amount of iodine was added and the solution left for half an hour and then the titration completed. Error was -0.01% so phosphite does not affect the titration.

The method now followed was to allow phosphorus and iodine to react until all the iodine was gone and then to shake up the solution with aq $\text{Na}_2\text{S}_2\text{O}_3$ + 5 cc dil HCl and transfer it to a stoppered measuring cylinder. The aqueous layer was made up to a volume nearly twice that of the organic layer and a sample of it was then pipetted out and titrated with aqueous iodine and starch indicator. In this way the apparent amount of thiosulphate in the aqueous layer could be determined.

At first the solvent used for the phosphorus and iodine was hexane and the results came out high by anything from 1 to 12%. A blank carried out with hexane, a little P_2O_5 and no phosphorus came out correct to 0.0%. As it had been decided for other reasons to use carbon tetrachloride as solvent in future carbon tetrachloride was substituted for the hexane. This gave the organic liquid as the bottom and not the top layer.

First a solution of phosphorus in carbon tetrachloride was shaken with $\text{Na}_2\text{S}_2\text{O}_3$ + 5 cc dil HCl and the thiosulphate titrated as before but results from 1 to 5% high were obtained. It was thought that

it might be possible to remove all the phosphorus by washing the aqueous layer with carbon tetrachloride. This was tried as the previous high results were put down to the presence of some phosphorus in the aqueous layer. At first two washings using 10 ccs CCl_4 each time (aqueous layer approx. 70 cc) were used, the CCl_4 being removed by means of a separating funnel, and then the aqueous solution run into a measuring cylinder as before. The result was 4% low. Repetition using only one washing gave result 3% low and use of carbon disulphide as wash liquid also gave low results. Using the same method with no phosphorus present low results were again obtained indicating loss of thiosulphate. Instead of separating the carbon tetrachloride and aqueous layers addition of carbon disulphide was tried in the hope this might remove all phosphorus from the aqueous layer without taking out any thiosulphate. To prevent loss of thiosulphate the aqueous layer was made much larger than the organic layer. Two solutions of phosphorus in carbon tetrachloride was taken and treated with thiosulphate in this manner but the apparent amount of this sulphate came out 7 and 9% high. Blank experiences were now performed shaking phosphorus solution with acidulated water. A little iodine was required when the aqueous layers were titrated and there did not seem to be much hope of establishing satisfactory partition coefficients.

It was thought that addition of dil NaOH to the sample of the aq. layer taken for analysis would remove all phosphorus, by converting it to phosphorus and hypophosphite without having any effect on the thiosulphate. The solution could then be made acid and titration carried out as before. This was tried, a very slight smell of phosphine being produced on addition of the alkali. In the first experiment coal gas was used to remove the phosphine and a result 3% high was obtained. In the second experiment the solution was warmed to 50°C to remove the phosphine and a result of 9% high was obtained. Repetition with a smaller amount of phosphorus gave a result 4% high. It was hoped that passing air through the alkaline sample in the cold might suffice, but the apparent amount of thiosulphate present was found to be 4% high.

This pointed to the errors being due to direct action of phosphorus on thiosulphate, to iodine being taken up by hypophosphite, or to both these effects. On consulting solubility tables it was found that cadmium hypophosphite is insoluble in water but is decomposed by dilute acids, whereas cadmium thiosulphate is soluble in water to about 1%. Accordingly it was thought that a cadmium salt might be used to precipitate thiosulphate. Cadmium bromide was the only salt of cadmium which seemed to be at all suitable. The phosphorus in carbon tetrachloride was /

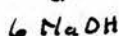
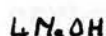
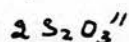
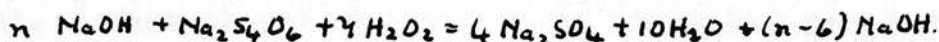
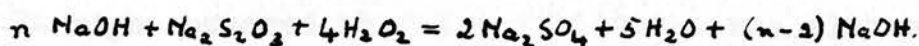
was shaken with thiosulphate and 5 cc dil HCl as before and a sample of the aqueous layer taken and made alkaline with 15 cc dil NaOH. After 10 minutes the solution was neutralised with HCl and made just alkaline to phenolphthalein with NaOH. Excess 10% aq. Cd Br₂ was added and the precipitate filtered and washed with Cd Br₂ solution. 5 cc dil HCl were added to the filtrate and on trititation the result was 4% high. Repetition gave a result 6% high and using sat. aq. Cd Br₂ a result 21% high was obtained. Cu SO₄ was thought of as likely to remove the hypophosphite but it gave no precipitate at all.

In view of the previous erratic results and the undesirability of using a pipette in the ordinary way with phosphate it was decided to shake up the solution in a separating funnel, run of the carbon tetrachloride, was once with 10 ccs carbon tetrachloride and titrate the whole of the aqueous layer. This was tried using 15 ccs Na₂S₂O₃ and similar amounts of phosphorus in carbon tetrachloride. In none of five cases were the results high by more than 0.1 cc apparent thiosulphate and usually they were only 0.05 cc high. Using aqueous phosphite solution as well as phosphorus the errors were of a similar order. This was very satisfactory, but when phosphorus and iodine solution in carbon tetrachloride were allowed to react until all the iodine was gone and were then treated in the same way as above /

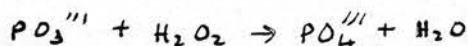
above, the apparent amount of thiosulphate present began to be as much as 1 cc too high, nor did the size of the discrepancy appear to be simply related to the amount of iodine or phosphorus initially present. A solution of phosphorus in carbon tetrachloride was left exposed to light and air for half an hour then shaken up with $\text{Na}_2\text{S}_2\text{O}_3$ and the thiosulphate determined as above. Only a very small error appeared. The presence of iodine in the organic layer would seem to be responsible for the high results due either to hydrolysis of iodide or activation of phosphorus by iodine. If free iodine was being left over results would have been low not high. Carrying out all operations with solutions saturated with carbon dioxide and in an atmosphere of carbon dioxide had no effect on the discrepancies. Further attempts at removing free phosphorus were made by adding concentrated aluminium chloride to precipitate any colloidal free phosphorus before the organic liquid was removed but this caused no improvement. It was also attempted to precipitate thiosulphate with barium chloride but no precipitate could be obtained even in presence of alcohol.

Another possible method of estimating thiosulphate is to add a definite amount of NaOH to the neutral solution and oxidise with H_2O_2 . NaOH is used up in the oxidation and the amount used can be determined with standard alkali. This method is usually employed for thiosulphate alone but since tetrathionate is /

is oxidised using a different amount of NaOH it was thought that it might be possible to use this method here. By first heating with NaOH and then neutralising the solution it was hoped to have all phosphorus as H_3PO_2 , H_3PO_3 and H_3PO_4 or salts of these acids and oxidation of these with H_2O_2 does not require any alkali.



If only PO_2''' , PO_3''' and PO_4''' are present



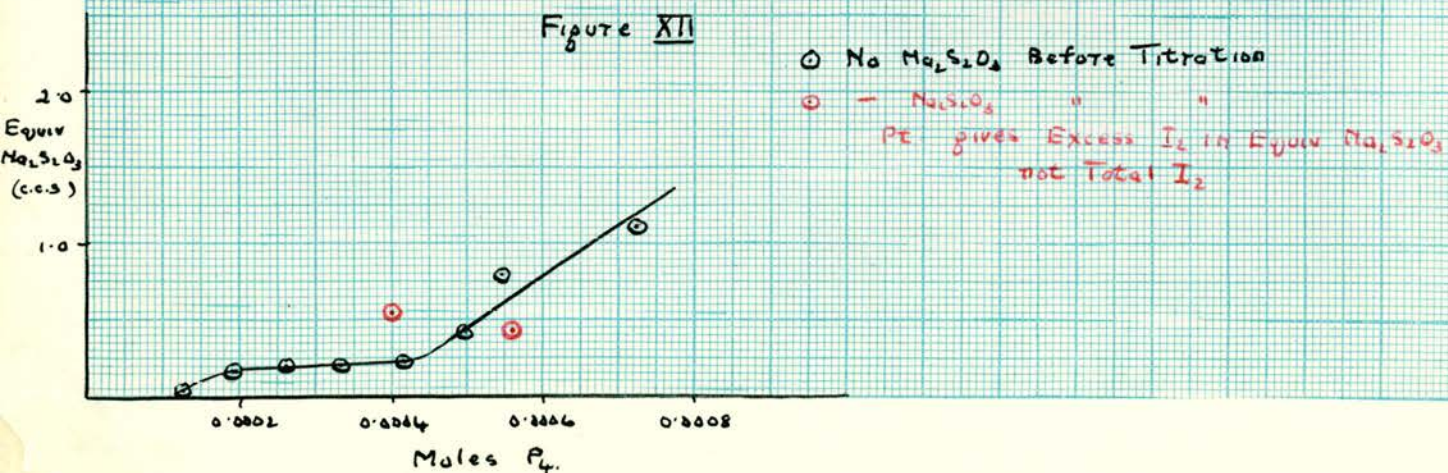
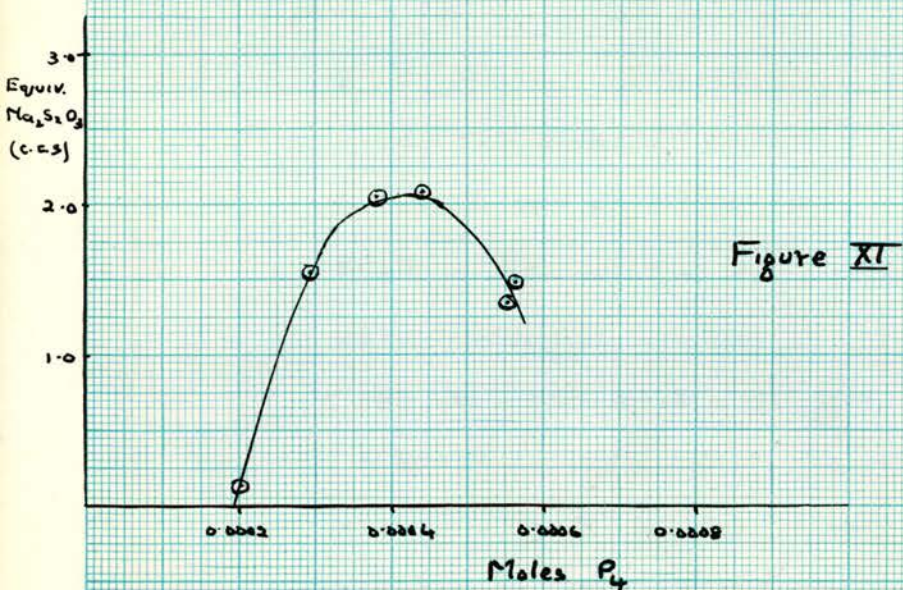
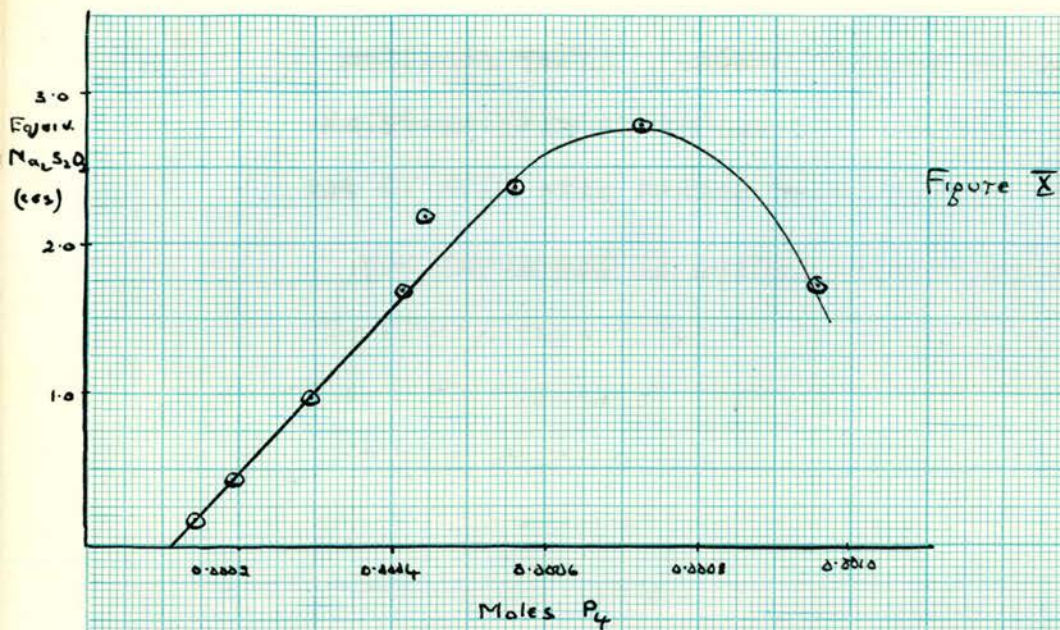
No alkali should be used or produced here.

$\frac{N}{20}$ NaOH and HCl solutions were used in conjunction with $\frac{N}{100}$ $\text{Na}_2\text{S}_2\text{O}_3$. It was found necessary to boil the solution for several minutes to complete the H_2O_2 oxidation. At first methyl red was used as indicator but as concordant results were not easily obtained phenol/^{red} was used. With this indicator the solution to be titrated with acid is first boiled and this is continued until, with a slight excess of acid present, the colour is not reversed on continued boiling i.e. all carbon dioxide has been expelled, then a few drops of alkali are added until the pink colour returns. The method was to make the thiosulphate slightly /

slightly acid to phenol red and pass air through the cold solution for a few minutes to expel carbon dioxide. The solution was then carefully neutralised and a known volume of NaOH added. Excess H_2O_2 was then added the solution boiled for several minutes and then titrated with HCl as described above. With $\text{Na}_2\text{S}_2\text{O}_3$ results were constant to 0.2% but results 1 or 2% high appeared when tetrathionate was also present. When phosphorus solutions which had reacted with solution of iodine in carbon tetrachloride were used very large errors appeared. Solutions were washed with carbon tetrachloride and warmed with NaOH to remove free phosphorus and care was taken to expel all carbon dioxide before adding alkali and H_2O_2 . Either interference is due to lower oxides of phosphorus or to direct action of phosphorus on thiosulphate.

An attempt was made to titrate thiosulphate using a potentiometric method.⁵⁶ This worked well with no phosphorus present but when the thiosulphate had been shaken up with phosphorus-iodine solutions after complete removal of iodine had taken place the results were no better than those obtained by the usual method. It had been hoped that two sharp breaks in the voltage /cc I_2 graph would have been obtained but this was not found to be the case.

Finally an attempt was made to find an approximate correction curve. The method was to take a definite amount of iodine in carbon tetrachloride and add some phosphorus /



phosphorus in carbon tetrachloride. After reaction was complete the solution was shaken up with acidulated water and the aqueous layer washed once with 10 ccs CCl_4 and then tritated with iodine in the usual way. The iodine used, expressed as the equivalent amount of thiosulphate, was plotted against the amount of phosphorus initially present. Results are shown in Figures X. and XI. These curves did not give much hope of their being used as correction curves but it was decided to investigate the initial parts of the curve. These results are shown in Figure XII. It is to be noted that the two cases in which thiosulphate was added to the acidulated water before it was shaken up with the phosphorus solution are not concordant with the rest. It was decided to abandon the analytical method of attacking the problem and to see what could be done by visual inspection of the iodine colour. The difficulties would seem to be due chiefly to the products of hydrolysis of phosphorus iodides and also to some direct action of phosphorus on thiosulphate in presence of iodides.

Direct /

DIRECT COLOUR COMPARISON.

A number of small test-tubes were made from one length of 3/16" glass tubing and in them was placed a series of solutions of iodine in carbon tetrachloride. The concentrations of these were such that it was just possible to see a difference in colour between two neighbouring solutions when the test-tubes were arranged in front of an illuminated opal plate. One set of such solutions was as follows :-

<u>Table V.</u>	
1. $I_2=0.00360$ moles I_2 /litre	2. $O_2=0.00324$ moles I_2 /litre.
3. 0.00292	3. 0.00257
5. 0.00226	6. 0.00195
7. 0.00167	8. 0.00144
9. 0.00124	10. 0.00106
11. 0.00091	12. 0.00079
13. 0.00068	14. 0.00058
15. 0.00050	16. 0.00042

The reactions were carried out in a series of large pyrex stoppered test-tubes which were blackened on the outside when dark reactions were being investigated. The test-tubes could also be kept at any desired temperature by thermostats. The reactions were followed by removing samples at intervals by dipping into the reaction vessel, a short length of the same glass tubing as had been used to make the test-tubes for the standard solutions. The colour of the sample removed /

removed was rapidly compared with the set of standards and an estimate of the concentration of iodine in the reaction vessel could thus be obtained. The investigation of the absorption of light by the products (page ⁴⁶) showed that this could be done. Since light accelerates the reaction colour comparison had to be done rapidly, it being frequently necessary to take a rough estimate first and a more accurate determination from a second sample taken immediately after the first. A series of such readings were taken during the course of any one reaction the error in each being from 10 to 20%, but ^{when} several were taken the error was lower. Errors of this order could be obtained by the analytical method, but colour comparison gave results much more quickly and without introducing moisture.

At first reactions were studied at 15°C and were started and timed in a similar manner to that used in the photocell work. It was found that the set of standards tended to change concentration after several weeks due to absorption of iodine by the stoppers, and it was usual to prepare a fresh set once a fortnight. This was thought to be more reliable than attempting to seal off the test-tubes or obtaining a set fitted with ground glass stoppers.

Carbon tetrachloride was used as solvent since there is no possibility of its ^{reacting with} taking up iodine and it is as near the ideal solvent as hexane. Hexane had shown /

Figure XIII

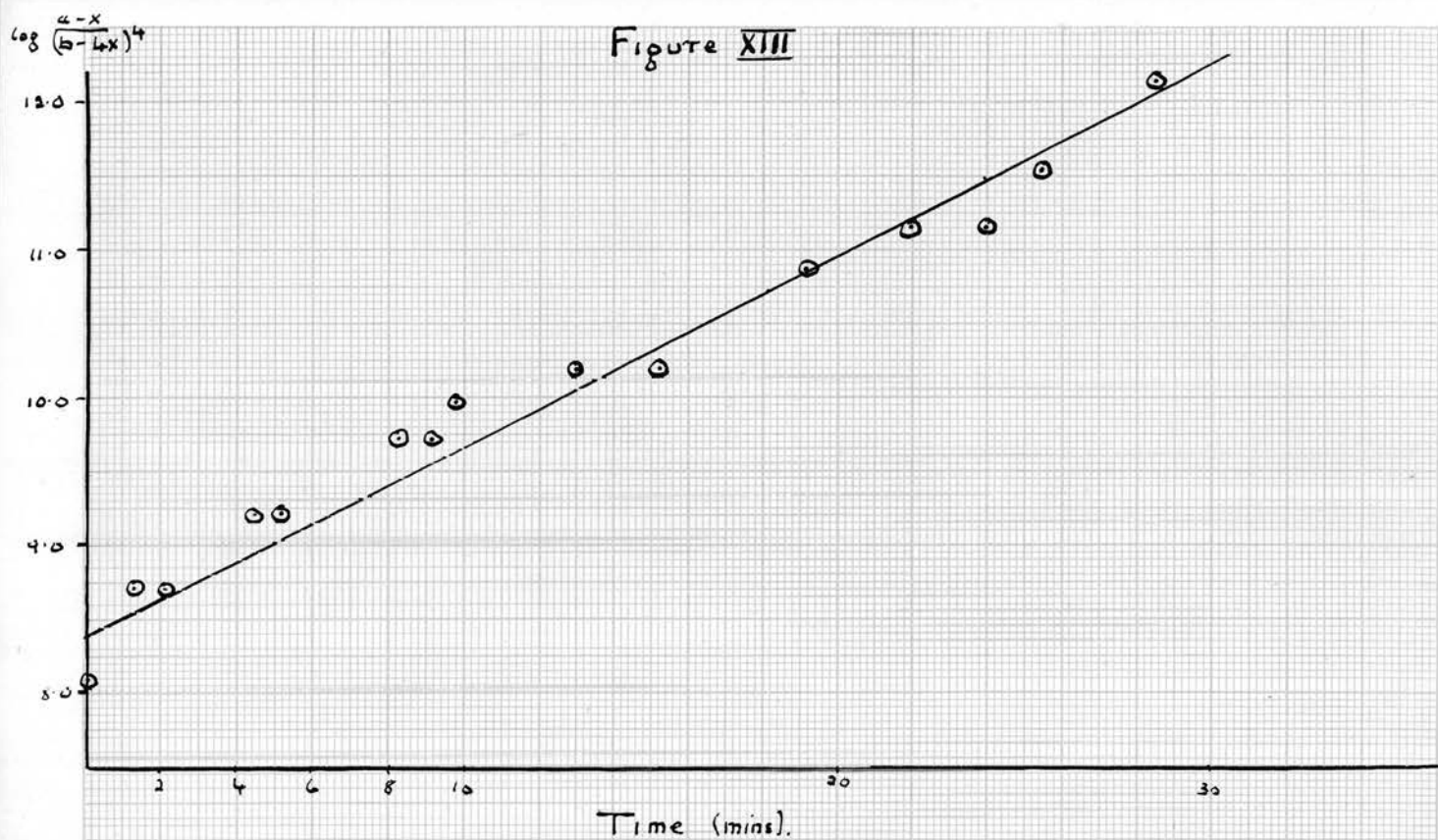
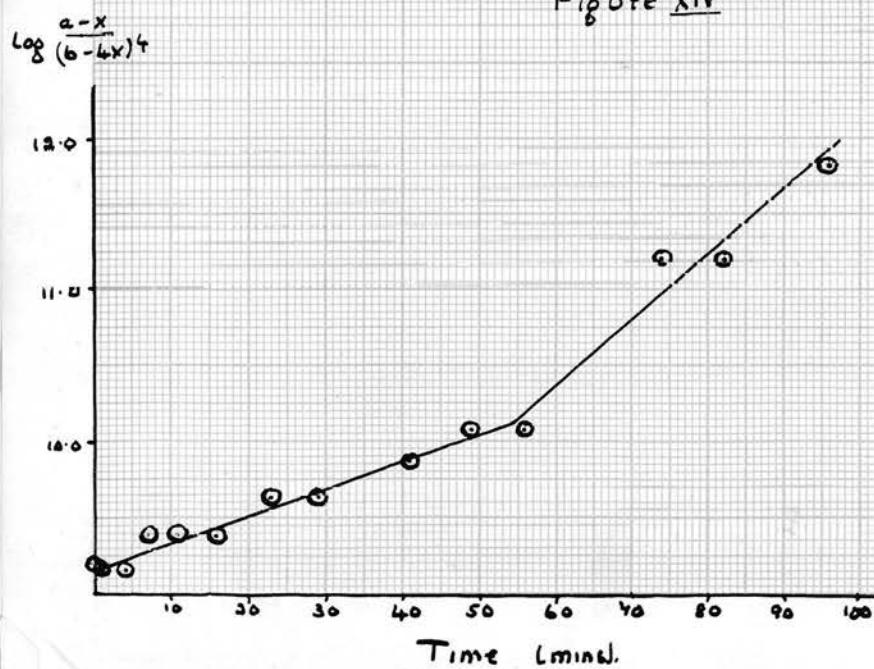


Figure XIV



shown no tendency to react with iodine but it does take up bromine, and since comparative work was to be carried out later with bromine it was thought to be preferable to use the same solvent throughout.

It was again found that the reaction went to completion and was affected by light, temperature etc. [as in hexane (page 45)]. The reactions were studied in the dark using A.R. carbon tetrachloride but no attempt was made to dry the solvent further. It was [again] assumed that reaction went straight to P_2I_4 and so phosphorus and iodine exist as P_4 and I_2 in CCl_4 the expression. was again obtained where

$$t = \frac{1}{k(b-4a)} \log \frac{a(b-4x)^4}{b^4(a-x)}$$

a, b and x have the same significance as before (page 42). This time the change in phosphorus concentration was not ignored and the full expression was used k being plotted against $\log \frac{(a-x)}{(b-4x)^4}$

$$t_2 - t_1 = \frac{1}{k(4a-b)} \left[\log \frac{(a-x_2)}{(b-4x_2)^4} - \log \frac{(a-x_1)}{(b-4x_1)^4} \right]$$

Figure XIII. is a sample of the results obtained. Occasionally graphs such as Fig. XIV. were obtained and these could not be accounted for and a few came out as in Fig XV. Here there is the possibility that the catalytic effect due to moisture present is being reduced, owing to drying produced by the reaction products. These formed only /

$$\log \frac{a-x}{(b-4x)^4}$$

Figure XV

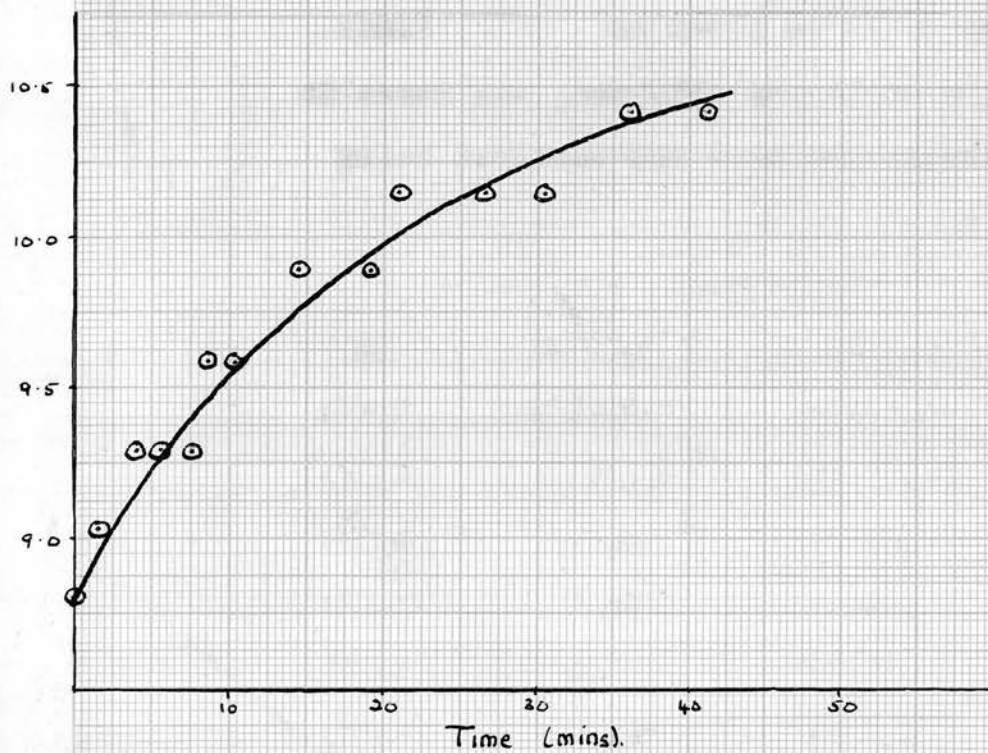
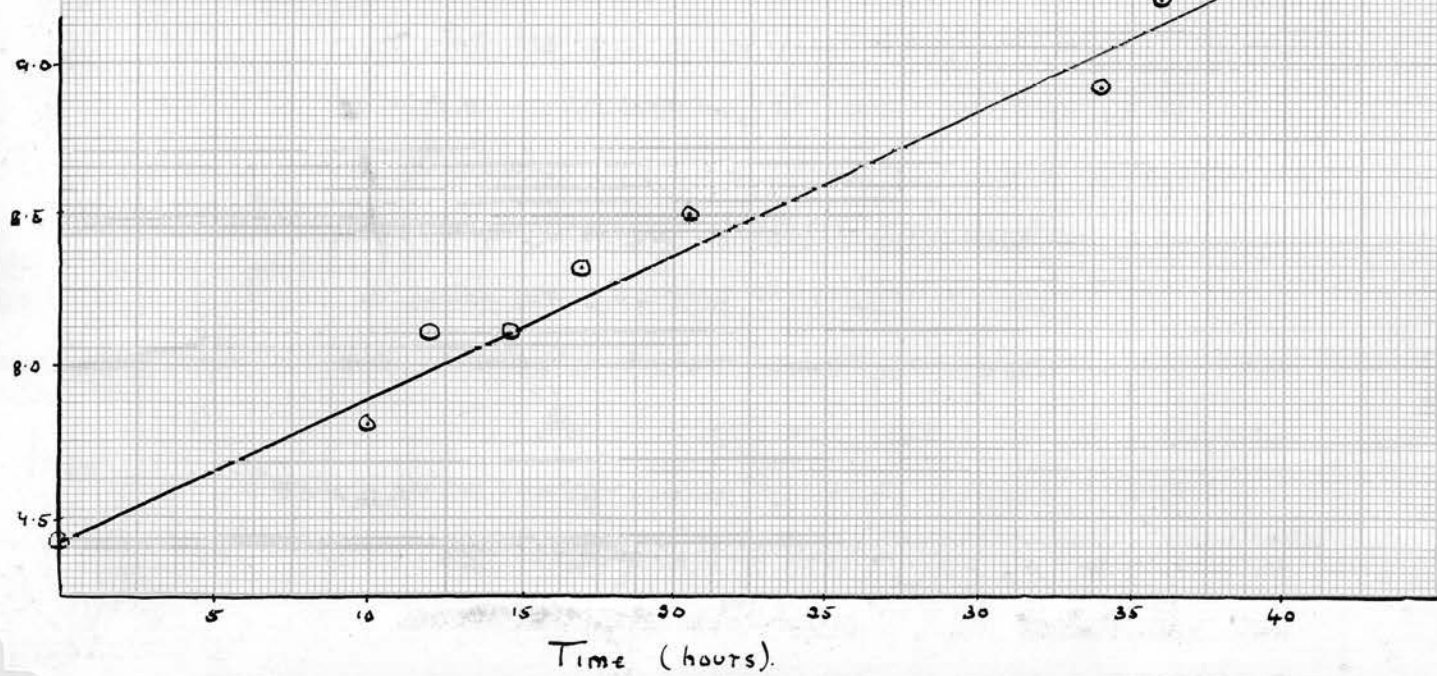


Figure XVI

$$\log \frac{a-x}{(b-4x)^4}$$



only a small proportion of the results and by far the largest number could be given as straight lines.

The following table was obtained, the cases in which straight line graphs were not obtained being disregarded.

Table 6.

<u>Conc. of P₄</u>	<u>Conc. of I₂</u>	<u>Volume</u>	<u>k</u>
0.0090	0.00206	25.8 cc.	0.140
0.0103	0.00158	33.7	0.100
0.0071	0.00275	19.3	0.220
0.0071	0.00137	38.8	0.184
0.0074	0.00176	30.2	0.177
0.0065	0.00099	53.7	0.053
0.0084	0.00151	55.2	0.080
0.0110	0.00132	40.2	0.088
0.00412	0.00153	34.7	0.052

The mean is 0.122.

The concentrations are expressed in moles P₄ or I₂ per litre and to obtain the time was expressed in seconds. The large variation in k was ascribed to differing amounts of moisture. This variation is less than that in the results obtained with the photocell (Table 4) and all the results here are 60 times less than the previous ones due probably to the entire absence of light.

The following results were obtained with glass rods in the test-tubes and frequent shaking. It was calculated that the surface area had been increased /

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increased three times.

Table 7.

<u>Conc of P₄</u>	<u>Conc of I₂</u>	<u>Volume</u>	<u>k</u>
0.0069	0.00140	37.5 cc.	0.100
0.0081	0.00149	35.7	0.181
0.0049	0.00177	29.9	0.181
0.0053	0.00135	39.2	0.177
0.0086	0.00220	24.1	0.186
0.0046	0.00181	29.3	0.146
0.0067	0.00228	27.6	0.133

Mean $k_2 = 0.158$.

This increase is within the large variation of the results and if real can possibly be ascribed to heating due to friction of the rods on shaking.

The following results were obtained at 35°C with no glass rods.

Table 8.

<u>Conc of P₄</u>	<u>Conc of I₂</u>	<u>Volume</u>	<u>k</u>
0.0051	0.00196	32.1 cc.	0.198
0.0060	0.00248	25.4	0.142
0.0098	0.00210	29.9	0.076
0.0061	0.00183	34.3	0.113
0.0068	0.00168	37.4	0.132
0.0038	0.00186	33.8	0.168

Mean k is 0.138.

Again the increase in k is insignificant. The mean value lies between that at 15°C and that at 15° / 15

15°C with glass rods present, but the variations from the mean make it impossible to say anything except that the change is very small.

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It was found that alcohol and ether had a much greater accelerating effect than moisture. The vessels used had been dried with alcohol, ether and the air blast but only traces of these solvents would be left behind. It was decided to attempt to obtain absolutely dry solution and after various trials it was found that the following method gave results which were fairly constant and much lower than those already cited.

The reaction vessels and pipettes were dried with alcohol, ether, and the air blast and then heated in the steam oven for several minutes. All pipettes were used with a CaCl_2 guard tube to prevent moisture passing into them. The phosphorus solution was prepared as described on page 23 using A.R. carbon tetrachloride which had been dried over P_2O_5 . The iodine solution was made by dissolving resublimed iodine in A.R. carbon tetrachloride and was kept over P_2O_5 . The dried reaction vessel was filled with carbon dioxide as before and then the phosphorus solution run in and 2 or 3 gms P_2O_5 added. This was left in the thermostat for 2 hours and then the iodine added. Reactions now took from 20 to 40 hours whereas before they had taken several minutes. It was found necessary to take a few readings one day and /

and the final readings the next day, thus gaps were ^{occurred} left overnight. In some cases two overnight gaps in the readings occurred Figure XVI.

The following is a summary of the results at 15°C.

Table 9.

<u>P₄ conc.</u>	<u>I₂ conc.</u>	<u>k.</u>
0.0058	0.00241	0.0021
0.0051	0.00316	0.0023
0.0047	0.00362	0.0020
0.0062	0.00208	0.0023
<u>0.0029</u>	<u>0.00277</u>	<u>0.0027</u>
0.0082	0.00305	0.0037
0.0077	0.00373	0.0031
0.0073	0.00243	0.0035
0.0068	0.00275	0.0040

The results above and below the line were obtained with different stock solutions of P₄.

Mean of 1st five = 0.0023 Mean of 2nd four = 0.0036

Mean k = 0.0029 for all results.

These results are much more consistent than before and it is to be noted that the second batch have slightly higher P₄ concs.

EFFECT OF DIFFERENT SOLVENTS.

In view of the small effect of temperature and surface area and the existence of large changes in rate /

type
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rate of reaction due to alcohol ether and moisture it was decided to investigate the action of solvents on the reaction. First an attempt was made to obtain quantitative results with alcohol. To 100 cc. of the purest alcohol obtainable 5 gms. NaOH were added and left overnight to polymerise any unsaturated compounds. The solution was then distilled, the distillate refluxed over calcium for 5 hours and redistilled. Solutions of alcohol in carbon tetrachloride could be made up from this as desired. In all calculations of the concentration of alcohol its density was taken as 0.70. The phosphorus solution and the required amount of alcohol were left over P_2O_5 for 3 hours with occasional shaking before the addition of iodine.

Table 10.

<u>Conc of alcohol</u>		<u>Conc of P</u>	<u>Conc of I_2</u>	<u>k</u>
moles C_2H_5OH /litre.	Vol %	moles/litre		
0.0018	0.0107	0.0049	0.00228	0.0023
0.0084	0.049	0.0059	0.00150	0.0028
* 0.019	0.116	0.0052	0.00148	0.0023
0.041	0.24	0.0053	0.00178	0.007
0.051	0.30	0.0067	0.00182	0.035
0.062	0.36	0.0055	0.00222	0.040
* 0.075	0.44	0.5041	0.00269	0.0025
0.085	0.50	0.0060	0.00152	0.48

* Much P_2O_5 in relation to total volume.

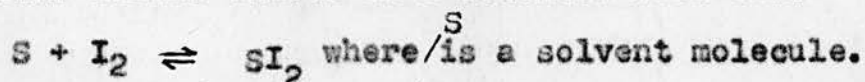
It is to be noted that the addition of much P_2O_5 in the cases marked caused a return of the result to normal /

normal and that the results are erratic. This would seem to indicate either that the effect is due to moisture being more easily incorporated in presence of alcohol or that P_2O_5 removes alcohol. In view of the care taken in drying the solution the first is unlikely. Some P_2O_5 was poured into the pure dried alcohol and it was completely dissolved with effervescence and evolution of heat. Since there was not enough moisture in the alcohol to do this P_2O_5 must react with alcohol and this will be the cause of the vagaries in the above results.

At this point the presence of water, alcohol, and ether had been shown to accelerate greatly the rate of reaction between phosphorus and iodine but the reason for this was not immediately obvious. The suggestion that the effect was due to moisture each time and that alcohol and ether only served to introduce it more readily into the carbon tetrachloride was not very tenable, in view of the care which had been taken to dry the solvents in the experiments with alcohol just described. It is known that in carbon tetrachloride iodine gives a violet solution whereas in alcohol, ether, and water it gives a brown solution. This fact suggested that the apparent speeding up of the reaction when these solvents are added to carbon tetrachloride might be spurious and due solely to their changing the colour of the solution. This did not seem likely to be the whole truth when the magnitude /

tude of the accelerating effect was considered but to test the matter solutions of iodine in carbon tetrachloride of about the concentration used in the previous work were taken and alcohol added. It was found that even with 2 or 3 times as much alcohol as carbon tetrachloride present the intensity of the colour of the solutions was little altered although the colour had changed to reddish brown. With the proportions of carbon tetrachloride and alcohol which had given the catalytic effect no change in tint could be detected. Hence the increase in reaction rate is real and not apparent.

It is generally considered that in the brown solutions iodine exists in a solvated form thus



This compound is practically non-existent in violet solutions but in brown solutions iodine exists almost entirely in the solvated form although the complex is so loose that iodine still exhibits all the characteristic reaction. It was decided to compare the colour of solution of iodine with the catalytic effect of the various solvents. The method was to mix wet solutions of phosphorus and iodine and add equal quantities of the mixture to two test-tubes, one containing wet carbon tetrachloride and the other an equal amount of wet carbon tetrachlorid plus a few drops of the selected solvent. The effect of the various /

various solvents could then be found by a comparison of the rates of reaction in the two test-tubes. Solutions saturated with water were used, since otherwise even approximate comparison of the dryness of solutions would have been difficult.

Results can be summarised.

Table 11.

<u>Large Increase in Rate</u>	<u>Small Increase</u>	<u>No Increase</u>
Alcohol	Benzene	Chloroform
Methyl alcohol	Toluene	Carbon Disulphide
Acetone		Hexane
Ether		Cyclohexane
Water (known already)		

and the colour of iodine solutions can be classified.

Table 12.

<u>Reddish-Brown</u>	<u>Intermediate</u>	<u>Violet(or Purple)</u>
Alcohol	Benzene	Chloroform
Methyl Alcohol	Toluene	Carbon Disulphide
Acetone		Hexane
Ether		Cyclohexane.
Water		

These two tables are identical, hence it was decided that the catalytic effect of the solvents is due to the solvated state of the iodine, but the effect cannot be accounted for by any precise explanation of the mechanism.

Further /

Further evidence against the effect being caused by mechanical introduction of moisture into carbon tetrachloride is given by the following solubilities taken from the International Critical Tables.

100 gms ether at 15°C dissolve	1.16 gms water
Chloroform	0.8
Carbon disulphide	0.22
benzene	0.05
toluene	0.06
hexane	0.014

This gives the "catalytic" solvents benzene and toluene as dissolving less water than the inactive chloroform and carbon disulphide.

Some experiments on the activity of iodine in organic solvents may now be mentioned. Feigl and Chargraff⁵⁹ studied the action of iodine on the silver derivative of saccharin. They found that brown solutions of iodine in ether, alcohol, dioxan, cyclohexanol and cyclohexene react to give AgI quantitatively, whereas violet solutions in carbon disulphide, carbon tetrachloride and light petroleum form only small amounts of AgI. The velocity of silver iodide formation depends on the solvent used for iodine, and they consider this to be due to the state of combination of the iodine and that such physical properties as dielectric constant of the solvent are only involved when they affect solvate formation. Feigl and Bondi⁶⁰ extended /

extended this to the study of activation of the inactive violet solutions in carbon disulphide and carbon tetrachloride using the same reaction as a criterion. They used as activators substances such as benzyl sulphide, pyridine, and quinoline, and found that with benzyl sulphide and carbon disulphide they could obtain a more active solution than using pure ether. All the substances which could be used as activators are known to form polyiodides and they consider that the activators act as co-ordination centres for the iodine to take part in the reaction.

It was decided to attempt to obtain a set of results which could further illustrate the activation effect. Alcohol, methyl alcohol, and acetone are all acted on by phosphorus pentoxide, but this reagent was not expected to have any action on ether. The ether was the purest obtainable and of density 0.717. It was left over sodium for two days then distilled and kept over P_2O_5 . The ether was used in the same way as the alcohol in the previous experiments and the results may be summarised. The P_4 and I_2 concentrations are in gm moles/litre and k is in the usual units.

Table 13. /

Table 13.

<u>P₄ conc.</u>	<u>I₂ conc</u>	<u>Ether (Vol %)</u>	<u>k</u>
0.0069	0.00190	0.26	0.0030
0.0061	0.00227	0.32	0.0034
0.0080	0.00200	2.8	0.018
0.0070	0.00279	3.6	0.114
0.0080	0.00188	4.9	0.36
0.0038	0.00338	6.3	1.05
0.0071	0.00234	6.5	0.19
0.0038	0.00323	8.9	0.70
0.0053	0.00486	9.0	0.93
0.0052	0.00316	11.7	2.1
0.0068	0.00294	13.6	2.1

These results show an increase in k with increasing ether but this is very irregular. Also, it was found that with concentration of phosphorus and iodine similar to the above and in presence of P₂O₅, solutions which had shown little change over several hours yet reacted completely in a few seconds when a drop of carefully dried alcohol or ether was added and the mixture shaken. This is difficult to reconcile with the above results where even with high percentages of ether reaction still took several minutes unless P₂O₅ is having some effect on the ether.

Results were also obtained with solution saturated with water and these are given below.

Table 14.

<u>P₄ conc.</u>	<u>I₂ conc</u>	<u>k</u>
0.0050	0.00309	0.101
0.0082	0.00292	0.112
0.0166	0.00275	0.078
0.0138	0.00432	0.144
0.0092	0.00327	0.116
0.0137	0.00284	0.083

Mean k is 0.106

These are of the same order as those obtained with solution where no special precautions had been taken to remove moisture (Table 6) yet there must be more moisture present in this case than there was then.

DISCUSSION OF METHOD.

So far the assumptions made have resulted in constants being obtained which are fairly consistent yet show some what large variations. Also there are the cases where a straight line graphs were not obtained, about 10% of the total number examined. An examination was made of the results obtained with carefully dried solutions, it being intended to try to plot the rate of change of iodine concentration against time and thus see if the ratio Rate/iodine conc was constant, the small change in phosphorus concentration being disregarded. Unfortunately the overnight /

omit at present

overnight gaps made this most untrustworthy, and in the 10% of the total where straight line graphs were not obtained it can be said that this ratio is definitely not constant, but sometimes increases rapidly and sometimes decreases rapidly.

It was decided to investigate the effect of using phosphorus solutions of higher concentrations, it having been noted that the solutions having the higher phosphorus concentration often gave higher constants, though this had not been so far capable of proof. Accordingly, stock solutions of higher concentration were prepared by saturating the carbon tetrachloride with carbon dioxide before warming it with phosphorus. In this way stock solutions of concentration as high as 0.04 moles P_4 /litre could be obtained where before concentrations of 0.01 only had been used. A drawback experienced with these solutions was that they tended to deposit phosphorus for several days after preparation presumably due to supersaturation, and it was only after daily filtrations through cotton wool for several days that they became sufficiently stable to be used.

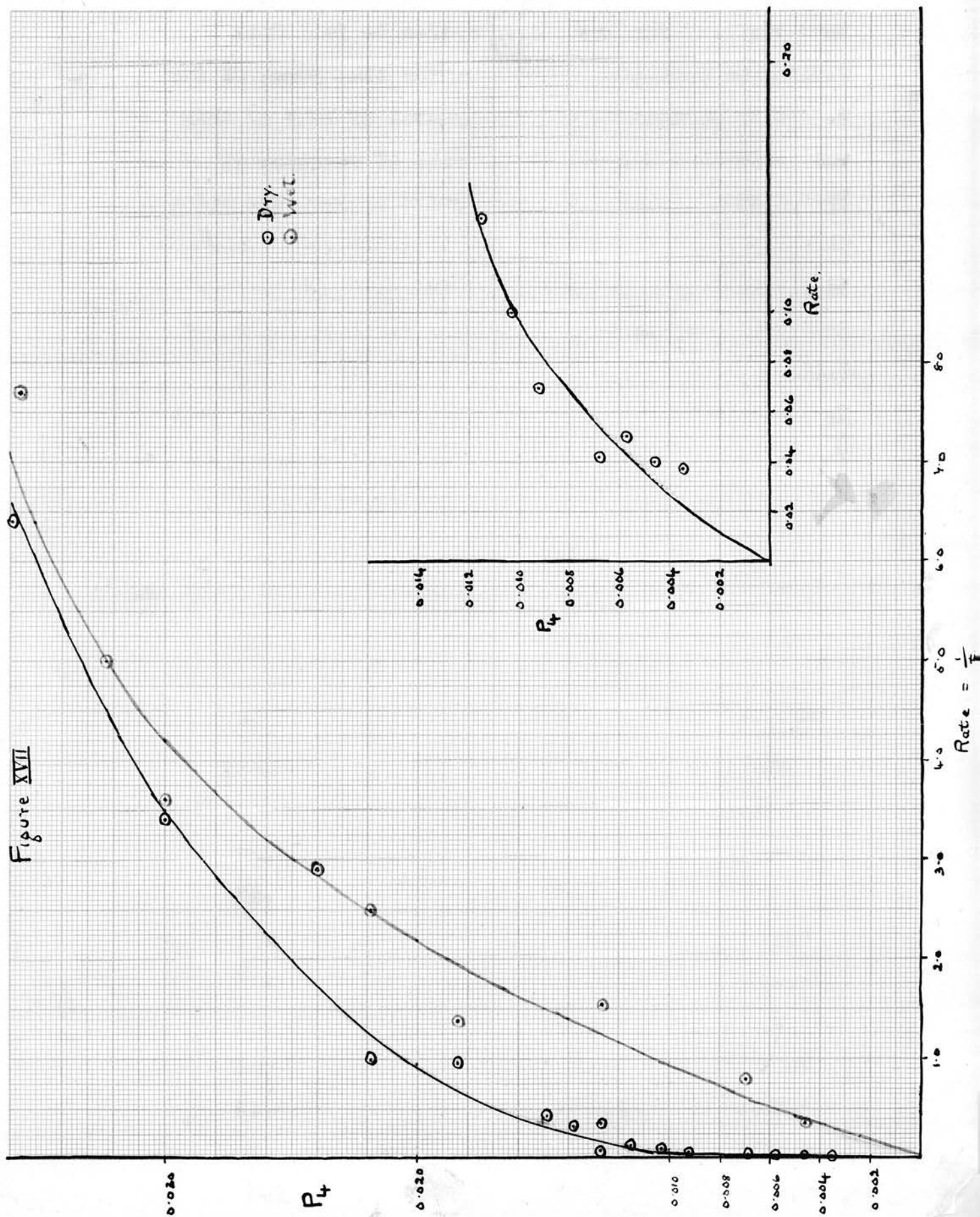
Two results obtained using concentration of phosphorus of about 0.01 against previous concentrations of 0.006 moles P_4 per litre, gave constants of about 0.01 whereas before they had been only 0.003. To make sure that the solvent contained no impurities it was taken, saturated with phosphorus, and excess liquid bromine /

bromine added to take up all the phosphorus. This was then shaken with conc NaOH till all the bromine was removed and distilled. Next it was shaken with conc H_2SO_4 , distilled, dried over CaCl_2 , redistilled and kept over P_2O_5 . With this as solvent it was found that with P_4 concentrations of the order of 0.01 constants of the order of 0.01, and with P_4 of the order of 0.015 constants of the order of 0.10 were obtained. It was thus seen that the previous assumptions were untenable with larger concentrations of phosphorus.

EFFECT OF VARYING PHOSPHORUS CONCENTRATION.

To obtain a better understanding of the reaction a series of experiments were carried out using the same initial iodine concentration and different phosphorus concentrations. The solutions were dried and studied at 15°C . First the initial phosphorus concentrations were plotted against the inverse of the half times, this being taken as a measure of the rate of reaction, but it was thought to be preferable to plot the phosphorus concentration against rate of reaction at a definite iodine concentration. To do this the inverse of the time required for the iodine concentration to decrease by 0.0001 moles I_2 /litre was taken as a measure of the rate. The rate at $\text{I}_2=0.00200$ was found by plotting iodine concentration against time in the neighbourhood of this concentration, and taking the time /

Figure XVII



time required for the concentration to fall from 0.00210 to 0.00190. This gave the time required for 0.0002 to be used up and the inverse of half of this was taken as a measure of the rate of reaction at $I_2=0.00200$. When this was plotted against the initial phosphorus concentration a graph was obtained, similar to the one which had been obtained when the inverse of the half time was taken as a measure of the rate. The initial iodine concentration was $I_2=0.00250$ moles I_2 /litre. The results are tabulated below, the phosphorus concentrations being given in \equiv moles P_4 /litre, and they are shown graphically in Figure XVII.

Table 15.

P_4 conc	Time for 0.0002 to be used up.	Rate = $\frac{1}{\text{time for 0.0001}}$
0.0035	54 mins	0.037
0.0046	50	0.040
0.0058	40	0.050
0.0069	48	0.042
0.0092	29	0.070
0.0103	20	0.10
0.0115	14.5	0.38
0.0127	22	0.091
0.0127	5.7	0.35
0.0138	6.2	0.32
0.0149	4.8	0.42
0.0184	2.1	0.96
0.0219	2.0	1.0
0.030	0.58	3.4
0.036	0.31	6.4

From this it is seen that the rate is not proportional to any simple function of the phosphorus concentration. It was thought possible that an expression of the type

Rate = $a P_4 (1 + b P_4)$ where a and b are constants might suffice, but this was found to be unsuitable. The rate might be expressed by

$$\text{Rate} = a P_4 + b P_4^2 + c P_4^3$$

but there would be no theoretical basis for such an expression.

Results were obtained at 10°C using the same initial iodine but with solutions saturated with water. These are shown in Table 16 and Figure XVII the rate at $I_2 = 0.00300$ again being used as criterion.

Table 16.

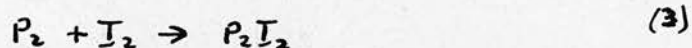
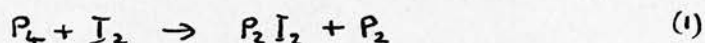
<u>P₄ conc.</u>	<u>Time for 0.0002 to be used up.</u>	<u>Rate = $\frac{1}{\text{time for 0.0001}}$</u>
0.0046	5.5 mins	0.36
0.0069	2.6	0.77
0.0127	1.30	1.54
0.0184	1.45	1.38
0.0219	0.80	2.5
0.024	0.70	2.9
0.030	0.55	3.6
0.032	0.40	5.0
0.036	0.26	7.7

These /

These gave a graph of the same general type as the one obtained with dry solutions but much flatter. The initial parts of both curves can be represented as straight lines and this is the region in which constants were being obtained in the previous calculations. At higher concentrations of phosphorus very rapid increase of reaction takes place.

Mechanism of Reaction.

In the hope of arriving at the meaning of the above results a careful examination of the possible reaction mechanism was made. First the reaction was considered as being



Assuming that a stationary concentration of intermediate is rapidly set up and maintained an expression for the rate of disappearance of iodine is arrived at as follows.

$$\frac{d(P_2I_2)}{dt} = k_1 P_4 \cdot I_2 - k_2 (P_2I_2) I_2 + k_3 P_2 I_2 = 0 \quad (a)$$

$$\frac{d(P_2)}{dt} = k_1 P_4 \cdot I_2 - k_3 P_2 \cdot I_2 = 0 \quad (b)$$

also

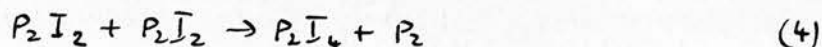
$$- \frac{d(I_2)}{dt} = k_1 P_4 \cdot I_2 + k_2 (P_2I_2) I_2 + k_3 P_2 \cdot I_2$$

eliminating P_2I_2 and P_2

$$- \frac{d(I_2)}{dt} = 4 k_1 P_4 \cdot I_2$$

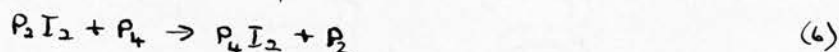
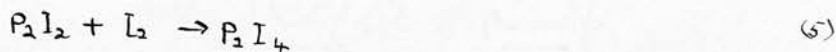
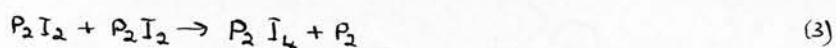
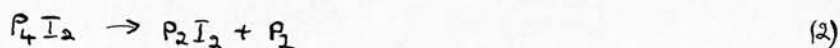
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As this expression is unsuitable the following scheme was tried.



which gives $-\frac{d(I_2)}{dt} = 3 k_1 P_4 \cdot I_2$

Finally the following set of equations was arrived at



Now $\frac{d(P_4 I_2)}{dt} = k_1 P_4 \cdot I_2 - k_2 (P_4 I_2) + k_6 (P_2 I_2) P_4 = 0 \quad (a)$

$$\frac{d(P_2 I_2)}{dt} = k_2 (P_4 I_2) - k_3 (P_2 I_2)^2 + k_4 P_2 \cdot I_2 - k_5 (P_2 I_2) I_2 - k_6 (P_2 I_2) P_4 = 0 \quad (b)$$

$$\frac{d(P_2)}{dt} = k_2 (P_4 I_2) - k_4 P_2 \cdot I_2 + k_6 (P_2 I_2) P_4 + k_3 (P_2 I_2)^2 = 0 \quad (c)$$

Adding (b) + (c)

$$2 k_2 (P_4 I_2) = k_5 (P_2 I_2) I_2$$

Also

$$\begin{aligned} -\frac{d(I_2)}{dt} &= k_1 P_4 \cdot I_2 + k_4 P_2 \cdot I_2 + k_5 (P_2 I_2) I_2 \\ &= k_1 P_4 \cdot I_2 + k_4 P_2 \cdot I_2 + 2 k_2 (P_4 I_2) \quad \text{from (d)} \end{aligned}$$

But from (b)

$$\begin{aligned} k_4 P_2 \cdot I_2 &= k_5 (P_2 I_2) I_2 + k_6 (P_2 I_2) P_4 + k_3 (P_2 I_2)^2 - k_2 (P_4 I_2) \\ &= 2 k_2 (P_4 I_2) + k_6 (P_2 I_2) P_4 + k_3 (P_2 I_2)^2 - k_2 (P_4 I_2) \quad \text{from (d)} \\ &= k_2 (P_4 I_2) + k_6 (P_2 I_2) P_4 + k_3 (P_2 I_2)^2 \end{aligned}$$

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And $\therefore -\frac{d(I_2)}{dt} = k_1 P_4 \cdot I_2 + 3k_2 (P_4 I_2) + k_6 (P_2 I_2) P_4 + k_3 (P_2 I_2)^2$

but $k_2 (P_4 I_2) = \frac{1}{2} k_5 (P_2 I_2) I_2$ from (d)

$$\therefore -\frac{d(I_2)}{dt} = k_1 P_4 \cdot I_2 + \frac{3}{2} k_5 (P_2 I_2) I_2 + k_6 (P_2 I_2) P_4 + k_3 (P_2 I_2)^2$$

$$= k_1 P_4 \cdot I_2 + (P_2 I_2) \left\{ \frac{3}{2} k_5 I_2 + k_6 P_4 \right\} + k_3 (P_2 I_2)^2 \quad (e)$$

But $(P_4 I_2) = \frac{k_5}{2k_2} (P_2 I_2) I_2$ from (d)

+ from (a)

$$k_1 P_4 \cdot I_2 - \frac{k_1 k_5}{2k_2} (P_2 I_2) I_2 + k_6 (P_2 I_2) P_4 = 0$$

$$\therefore k_1 P_4 I_2 = (P_2 I_2) \left\{ \frac{k_5}{2} I_2 - k_6 P_4 \right\}$$

$$\therefore (P_2 I_2) = \frac{k_1 P_4 \cdot I_2}{\frac{k_5}{2} I_2 - k_6 P_4}$$

Hence

$$-\frac{d(I_2)}{dt} = k_1 P_4 \cdot I_2 + \frac{k_1 P_4 \cdot I_2 \left(\frac{3}{2} k_5 I_2 + k_6 P_4 \right)}{\frac{k_5}{2} I_2 - k_6 P_4} + k_3 \left(\frac{k_1 P_4 \cdot I_2}{\frac{k_5}{2} I_2 - k_6 P_4} \right)^2$$

$$= k_1 P_4 \cdot I_2 \left[1 + \frac{\frac{3}{2} k_5 I_2 + k_6 P_4}{\frac{k_5}{2} I_2 - k_6 P_4} \right] + k_3 \left(\frac{k_1 P_4 \cdot I_2}{\frac{k_5}{2} I_2 - k_6 P_4} \right)^2$$

$$= \frac{k_1 P_4 \cdot I_2 (2 k_5 I_2)}{\frac{k_5}{2} I_2 - k_6 P_4} + k_3 \left(\frac{k_1 P_4 \cdot I_2}{\frac{k_5}{2} I_2 - k_6 P_4} \right)^2$$

$$= 4 I_2 \frac{k_1 P_4 \cdot I_2}{\left(I_2 - \frac{2 k_6}{k_5} P_4 \right)} + \frac{4 k_3}{k_5^2} \left(\frac{k_1 P_4 \cdot I_2}{I_2 - \frac{2 k_6}{k_5} P_4} \right)^2$$

\therefore Rate of I_2 disappearance

$$= -\frac{d(I_2)}{dt} = 4 I_2 \left(\frac{a \cdot P_4 \cdot I_2}{I_2 - b P_4} \right) + c \left(\frac{a P_4 \cdot I_2}{I_2 - b P_4} \right)^2$$

where $a = k_1$, $b = \frac{2k_6}{k_5}$ & $c = \frac{4k_3}{k_5^2}$

When $I_2 \gg bP_4$ this expression reduces to

$$4 a I_2 P_4 + c (a P_4)^2$$

and if c is sufficiently small it becomes $4a I_2 P_4$.

This is the form of the initial part of the P_4 /Rate curve, but with increase in P_4 conc the rate begins to increase more rapidly since bP_4 now becomes of size comparable to I_2 and the ratio

$$\frac{I_2}{I_2 - bP_4}$$

becomes greater than unity. Since the square of this increases even more rapidly, it is possible for the second term in the expression for the rate to increase, and finally to do so very rapidly and become much larger than the first term. When bP_4 becomes greater than I_2 the first term will become negative but the whole expression will still be positive due to the second term being larger and involving a negative quantity squared.

First of all it was decided to find what values of a , b and c fitted the P_4 /rate curve. The best values for dry solutions were

$$a = 100 \quad b = 0.04 \quad c = 0.06$$

and these gave agreement with experiment as shown below.

Table /

Table 17.

<u>P₄</u>	<u>Rate (exp)</u>	<u>Rate (calc)</u>
0.0050	0.036	0.050
0.0100	0.098	0.104
0.0150	0.36	0.29
0.0200	0.94	0.94
0.0250	2.0	1.9
0.0300	3.5	3.4
0.0350	6.0	9.0

All these are well within the possible error.

For wet solutions the results in Table 18 were obtained using

$$a = 10,000 \quad b = 0.01 \quad c = 0.00001.$$

Table 18.

<u>P₄</u>	<u>Rate (exp.)</u>	<u>Rate (calc.)</u>
0.0050	0.45	0.44
0.0100	0.96	0.95
0.0150	1.5	1.6
0.0200	2.2	2.3
0.0250	3.0	3.1
0.0300	4.2	4.1
0.0350	6.4	5.2

These are very satisfactory. It is to be noted that the final value for the rate is less than for the dry solution whereas experimentally very similar rates were found. It is probable that in this region the expression assumes stationary concentrations which are never completely established.

The effect of moisture seems to be greatly to increase the rate of the initial reaction, probably due to altering the reactivity of the I_2 molecules. The ratio of reactions (6) and (5) as given by b is only slightly reduced and the relative rate of reactions (3) and (5) is reduced considerably but it has to be borne in mind that the denominator is k_5^2 not k_5 . It is possible that reaction (3) takes place so readily in dry solutions that it is little affected by the presence of moisture, but that reactions (5) and (6) are taking place at comparatively slow speeds and can be considerably accelerated by an increase in the reactivity of P_2I_2 . This increase may be such as to speed up reaction (6) by an amount comparable with the increase in the rate of (5) in spite of the increase in reactivity of I_2 . This ignores the possibility of moisture affecting the reactivity of P_4 , but this is not likely to be large in comparison with the increase in reactivity of iodine, when the other reactions in which iodine takes part are borne in mind. (page 70.)

CATALYTIC PRODUCTION OF RED PHOSPHORUS.

The production of red phosphorus in the gas phase has been shown by Melville and Gray⁶¹ to proceed by formation of P_2 molecules and the recombination of these to give red phosphorus. It has also been /

19

been shown by King and Ludlam, that when ultra-violet light falls on phosphorus vapour P_2 molecules are produced and that these can combine at the walls of the vessel to give red phosphorus. Now reactions (2) and (6) of the above scheme can under suitable conditions give a continuous supply of P_2 molecules and it is possible for these to recombine to P_4 or, more likely, to give red phosphorus. These P_2 molecules will in general give red phosphorus and if I_2 molecules are still present the active P_2 molecules will react to give P_2I_2 but when the amount of I_2 has been reduced to a small value there will be a supply of P_2 molecules in solution. These may be expected to be much more reactive than P_4 molecules, and this may explain the difficulties experienced in the attempt to titrate thiosulphate after it had been shaken up with the products given by a P_4 - I_2 mixture. It will be remembered that on titrating the thiosulphate with iodine the apparent thiosulphate present was greater than that actually added.

An examination of the effect of iodine on the production of red phosphorus was made as follows. Two solutions of phosphorus were taken and placed in stoppered test-tubes, and enough iodine to give a very faint initial iodine colour was added to one sample. Both phosphorus solutions were of the same concentration.

First /

First of all a concentration of 0.04 mole P_4 /litre was used and the solutions left in the dark in test-tubes filled with CO_2 . After four days the solution to which iodine had been added contained a little pale yellow deposit which left a few red specks when shaken with water. Thus it must have been oxide of phosphorus with a few specks of red phosphorus. There was not enough iodine present to have given any noticeable iodide. The other solution only contained a few reddish-yellow specks insoluble in water and these were probably due to phosphorus coming out of solution since the solution was certainly saturated with phosphorus.

A second experiment was made with solutions containing $P_4=0.02$. After two days a little white precipitate was to be seen in the iodine test-tubes while the other remained clear. Air was blown into both. After another two days a copious white precipitate soluble in water was found in the solution containing the trace of iodine but the other only showed a slight milkyness. The presence of iodine thus promoted oxidation in the dark, due no doubt to the production of active P_2 molecules. Solutions in the dark always remained clear until all the iodine had gone, the P_2 molecules in this case reacting with iodine.

As already mentioned (page 45) the action of light is to speed up the rate of reaction and to cause /

cause the production of red phosphorus. Iodine in solution absorbs red and green light. According to Rabinovitsch and Wood⁶² the absorption of light by iodine dissolved in carbon tetrachloride and hexane produces primary dissociation into iodine atoms. Other solvents interact, more or less, with the iodine and the extinction coefficient may increase slightly on illumination. The detailed explanation of this fact is not simple but illumination is certain to increase the chemical activity of the iodine solution.

EFFECT OF VARYING IODINE CONCENTRATION.

According to the expression given reaction should proceed according to $4 I_2$ or P_4 if $\frac{I_2}{I_2 - bP_4} = 1$.

As I_2 decreases the rate of reaction will decrease according to $4 I_2$ or P_4 until I_2 becomes small enough for $\frac{I_2}{I_2 - bP_4}$ to begin to increase. When this happens the rate of reaction will increase and will become very large when I_2 approaches bP_4 . To test this a careful examination of the rate of disappearance of iodine throughout particular reactions was made. In no case was the percentage change in P_4 concentration very large, and so these could be taken as showing the effect of varying iodine concentration and keeping phosphorus concentration constant. A few of the cases examined are given below. The concentrations given for the iodine are of course the concentrations /

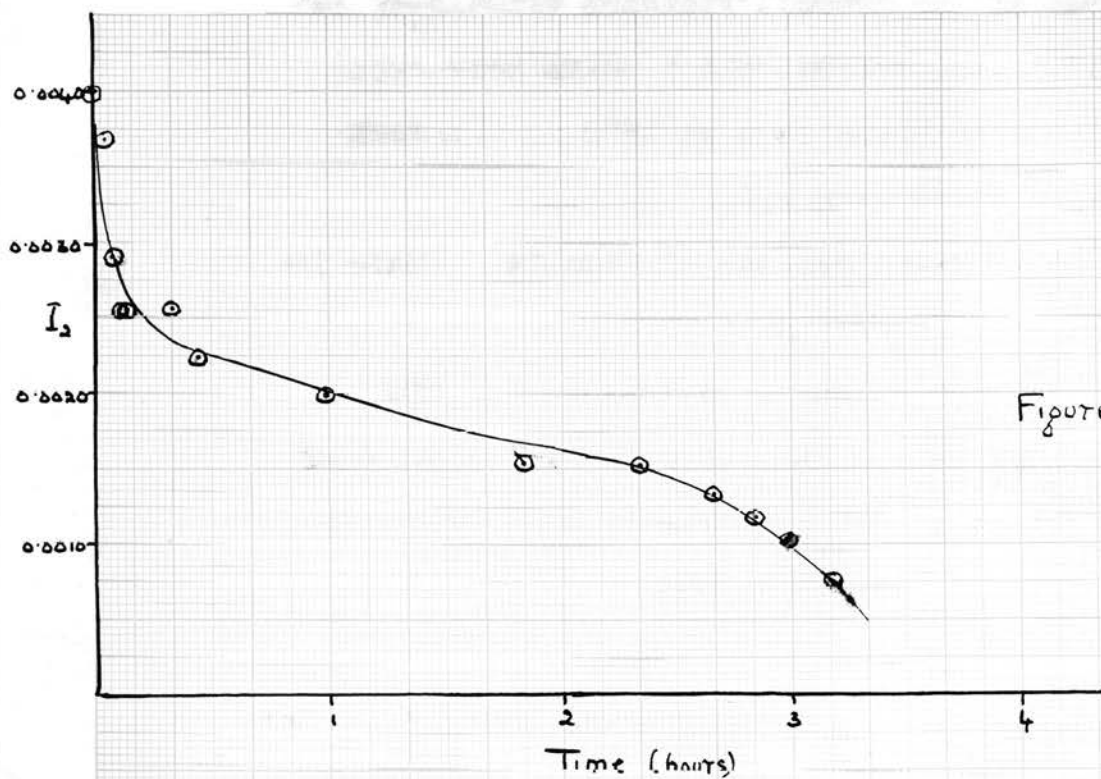
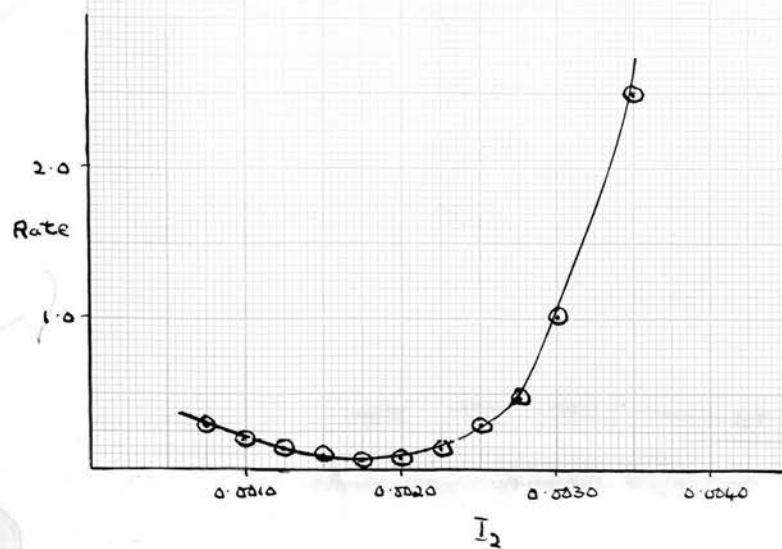


Figure XVIII



concentrations of the nearest standard solutions, except for the initial concentration which were accurately known. Reactions were at 15°C in the dark using solutions dried over P_2O_5 .

Table 19 contains one set of results. This is for $P_4=0.0084$ and $I_2=0.00398$ -:

Total fall in P_4 conc. in reaction is 12%.

Table 20 gives the rate of reaction calculated in the same way as in the experiments with constant I_2 and different P_4 concentrations.

Table 19.

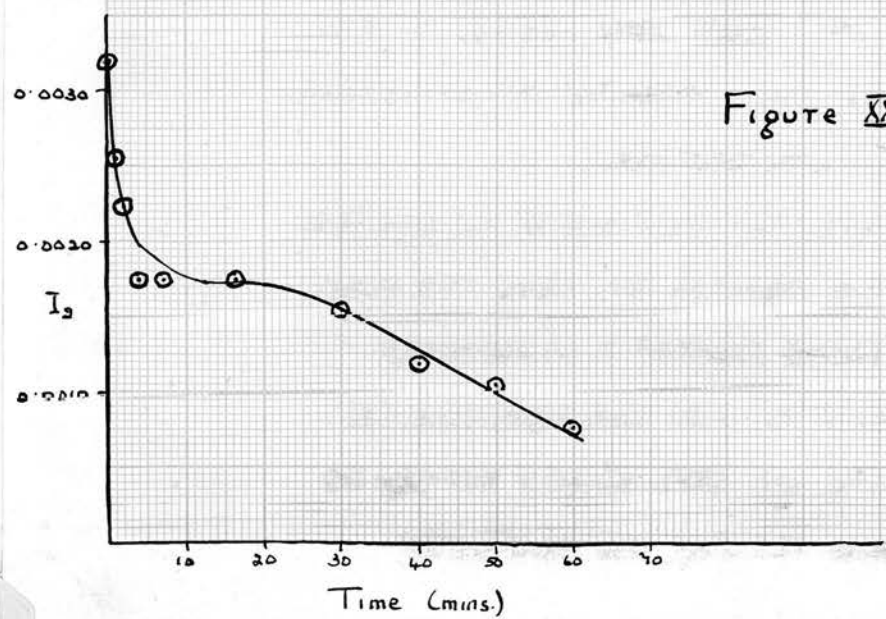
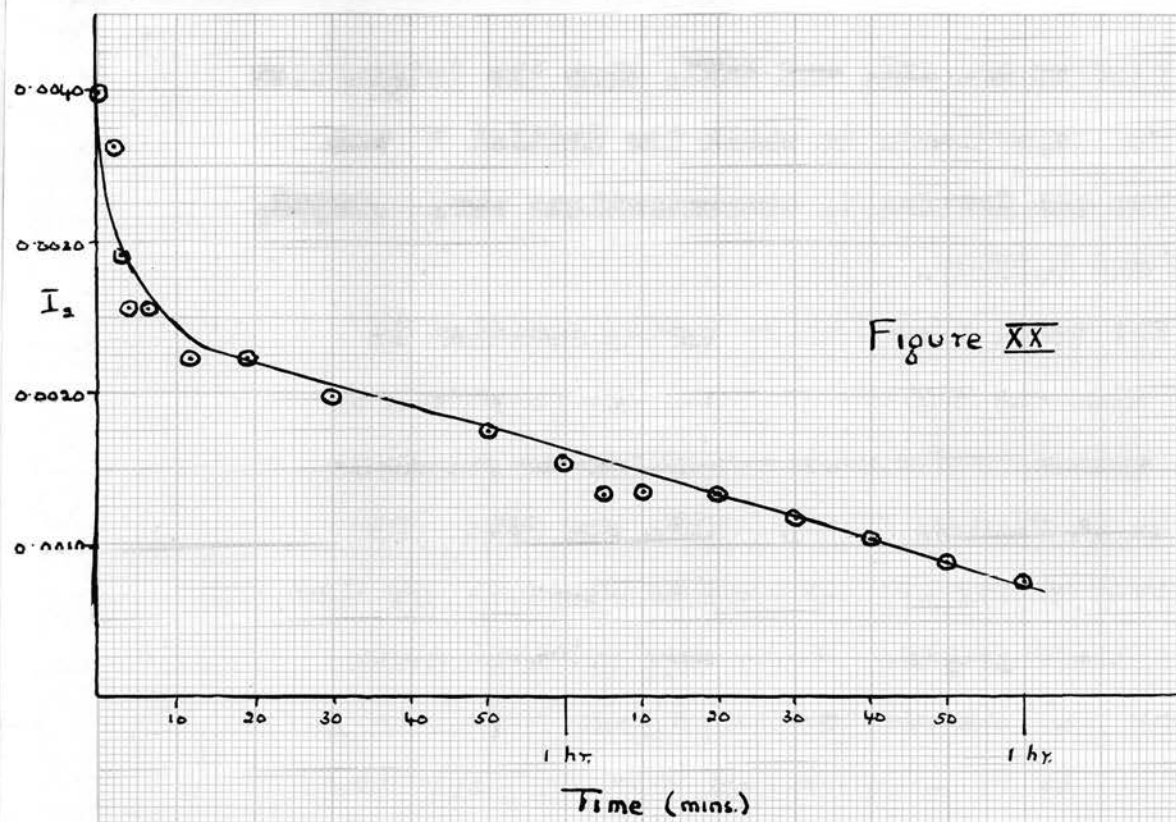
<u>Time</u>	<u>I_2 conc.</u>
3 m	0.00366
5	0.00290
7	0.00255
9	0.00255
20	0.00255
27	0.00224
59	0.00197
1 hr 50 m	0.00153
2 20	0.00153
2 40	0.00134
2 50	0.00118
3 00	0.00102
3 10	0.00075

Table 20.

<u>I_2 conc.</u>	<u>Rate= $\frac{1}{\text{time for } 0.0001}$</u>
0.00350	2.5
0.00300	1.0
0.00275	0.46
0.00250	0.29
0.00225	0.14
0.00200	0.07
0.00175	0.05
0.00150	0.08
0.00125	0.14
0.00100	0.20
0.00075	0.29

The graphs of iodine against time, and rate against iodine, are shown in Figures XVIII. and XIX.

Figures /



Figures ZX. XXI. and XXII. show the iodine/time curves for experiments in which the initial P_4 was 0.0163 but the initial I_2 concentrations were 0.00398, 0.00319 and 0.00199.

The total change in P_4 during reaction is only 6% with the highest I_2 conc. and is even less for the others. The rate/iodine curves for these are given in Figures XXIII., XXIV. and XXV. The theoretical values for the rate of reaction are also shown in these graphs. These were obtained using the values for the constants a, b, and c which give Table 21. It is to be noticed that initially there is a much more rapid fall in the rate than is to be expected from theory, but that once the rate of reaction has fallen to a value near the calculated one, it follows a course which is not very far removed from that calculated, except that the final increase in rate is not quite so large as was expected. The slight fall in P_4 conc will have some effect in decreasing the experimental rate here but no allowance for this was made in the calculations.

It was assumed when the derivation of the expression for the rate was carried out that the concentration of intermediates reached a stationary value immediately. In this case the experimental results for Figures XXIV. and XXV. should merely be the lower parts of Figure XXIII., and similarly Figures /

Figure XXII

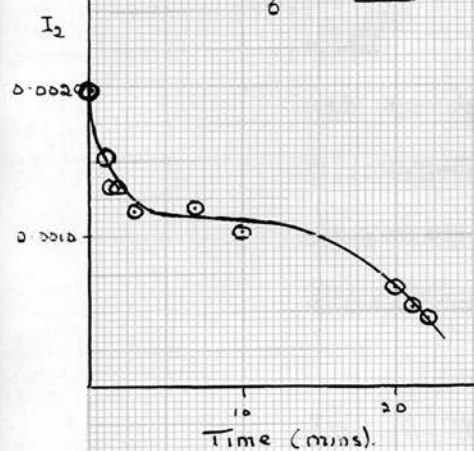


Figure XXIII

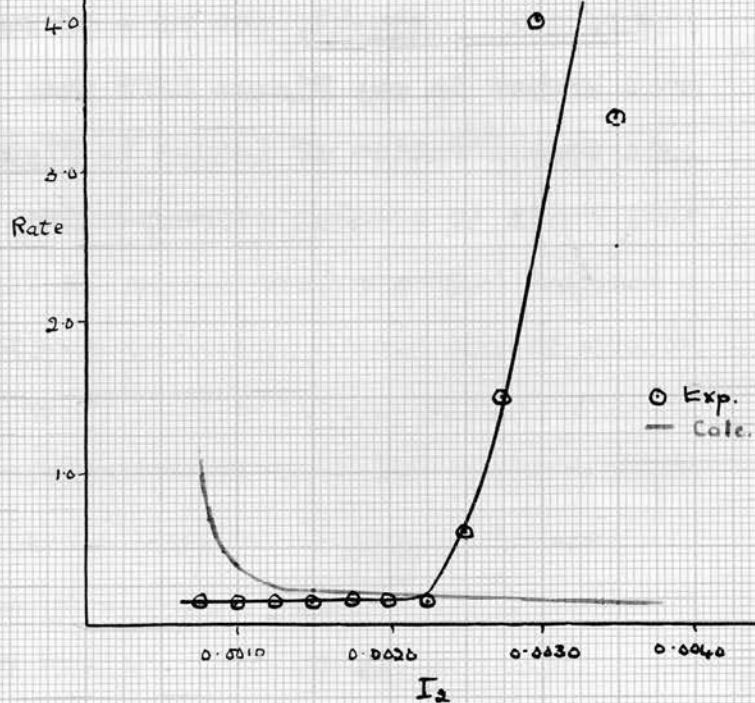


Figure XXIV

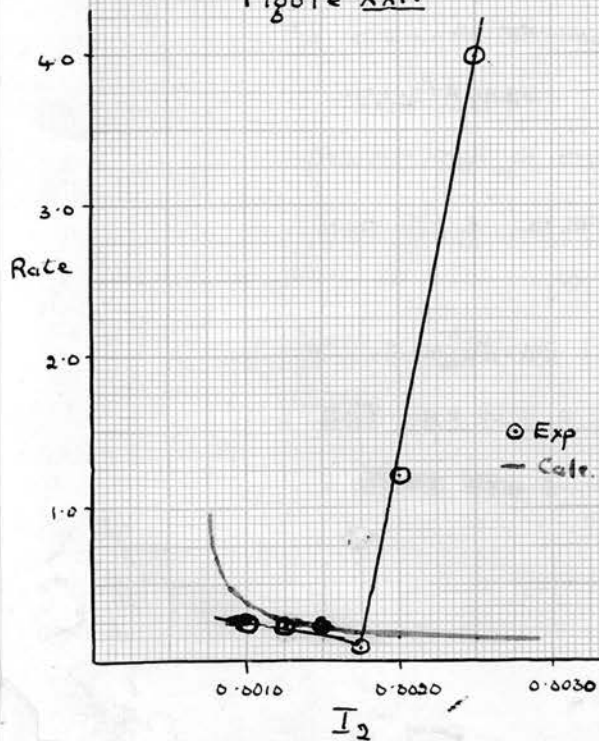
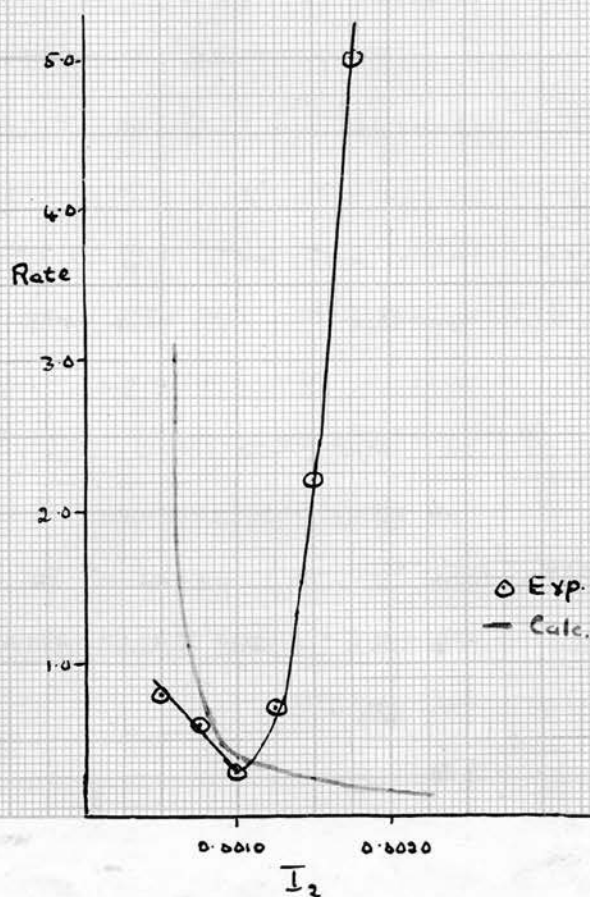


Figure XXV



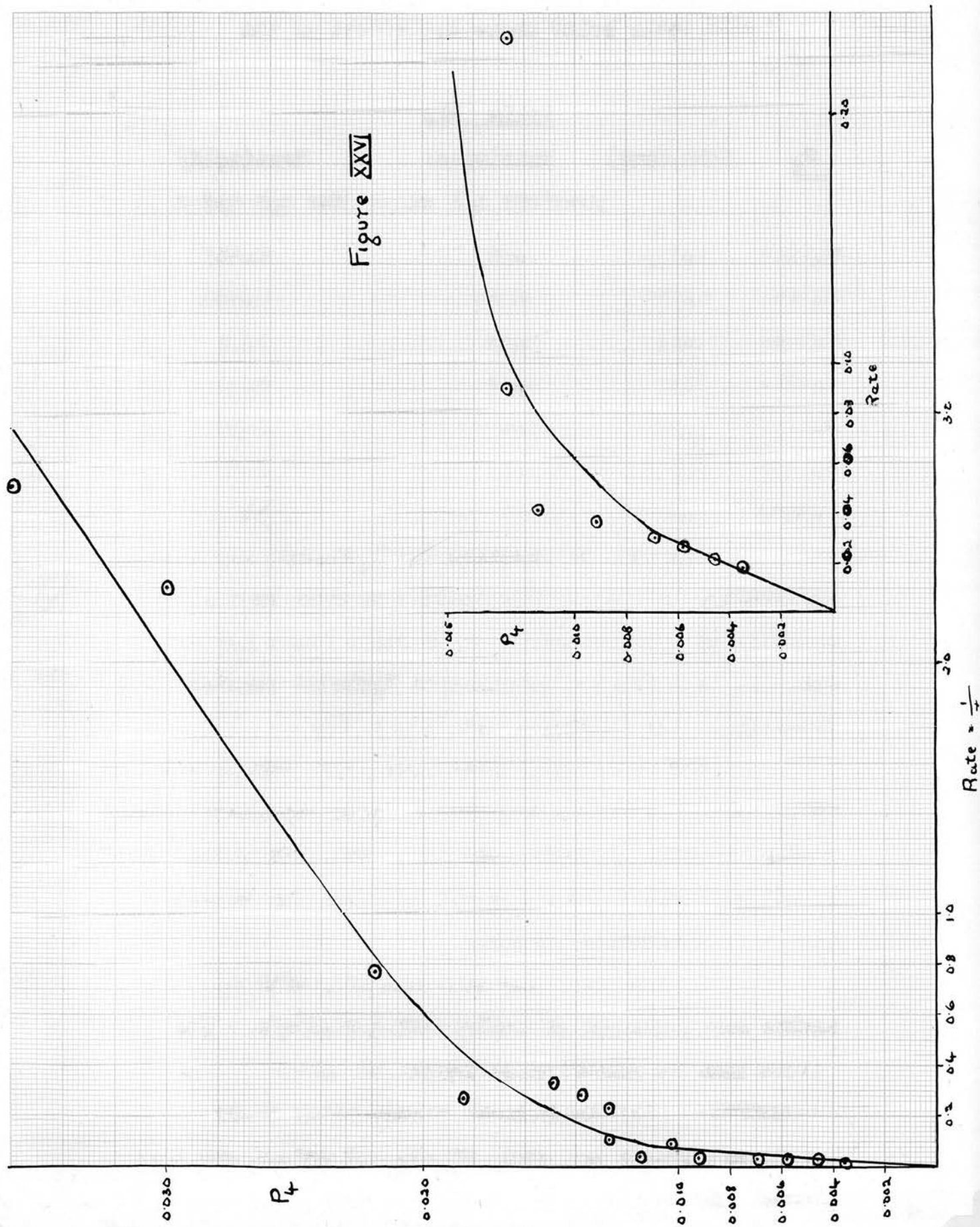
Figures XXI. and XXII. should merely be part of Figure XX. Actually the rate of reaction starts much higher in say Figure XXIV than it is for the same concentration of iodine in Figure XXIII., and then falls to a value corresponding to that found for a similar iodine concentration in Figure XXIII. This points to the setting up of an equilibrium after the reaction has proceeded a little way and a consequent slowing up of the rate of reaction. After reaction has reached a certain concentration of intermediates it follows the course predicted by theory.

The results in Table 15 and Figure XVIII. had been obtained taking the rate at $I_2=0.00200$. This is not far removed from the initial concentration of iodine, namely $I_2=0.00250$, and in view of the necessity for a little time to elapse before stationary concentrations are reached it is possible that at this iodine concentration the stationary concentrations of intermediates have not been obtained. Accordingly it was decided to plot the rate against P_4 concentration once more using the same experimental data and this time taking the rate at $I_2=0.00150$.

The graph thus obtained is seen in Figure XXVI. The former values of a , b and c did not fit this curve and it was found necessary to use $a=80$ $b=0.03$ and $c=0.06$.

The /

Figure XXVI



The table below shows the effect of the change.

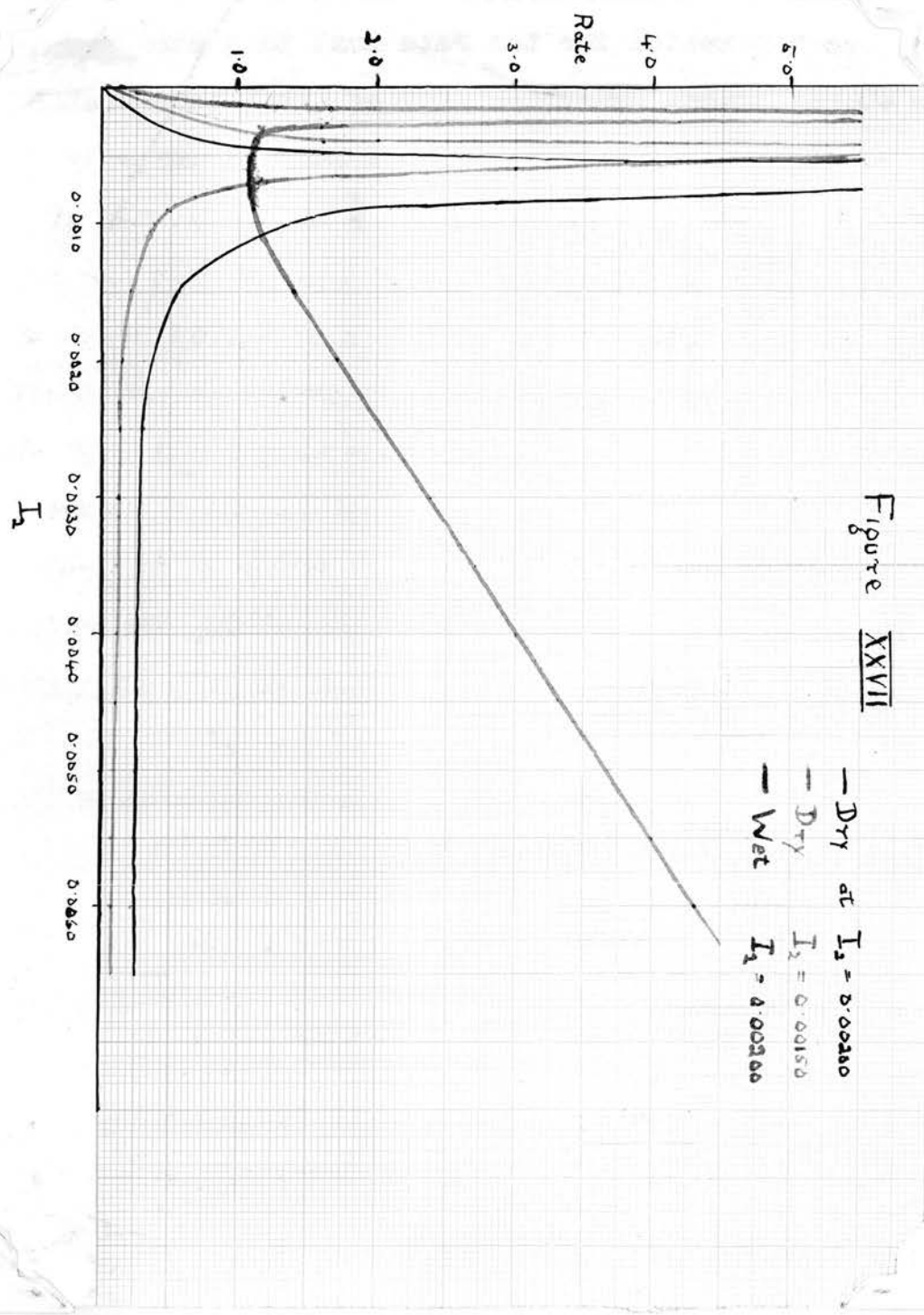
Table 21.

<u>P₄</u>	<u>Rate (exp)</u>	<u>Rate(calc)</u> previous a,b and c	<u>Rate(calc)</u> New a,b and c
0.0050	0.023	0.023	0.015
0.0100	0.062	0.120	0.066
0.0150	0.23	0.39	0.19
0.0200	0.60	1.13	0.45
0.0250	1.25	3.4	0.98
0.0300	2.0	4.9	2.2
0.0350	2.8	165	5.2

The rate of reaction for $P_4=0.0163$ and concentrations of iodine from 0.00600 to zero were calculated using the values of a, b and c found for wet solution, and for dry solution at $I_2=0.00200$ and 0.00150. These are shown in Figure XXVII.

The rates calculated from $a=100$ $b=0.04$ and $c=0.06$ are much larger than those found experimentally in Figures XXIII., XXIV., and XXV., but when $a=80$, $b=0.03$ and $c=0.06$ the rates are not very far removed from the experimental values.

A final test was made starting with an iodine concentration of 0.0079 and $P_4=0.0163$. The iodine/time and rate/iodine curves are shown in Figure XXVIII. The theoretical values using $a=100$ $b=0.04$ and $c=0.06$ and $a=80$, $b=0.03$ and $c=0.06$ are also shown. /

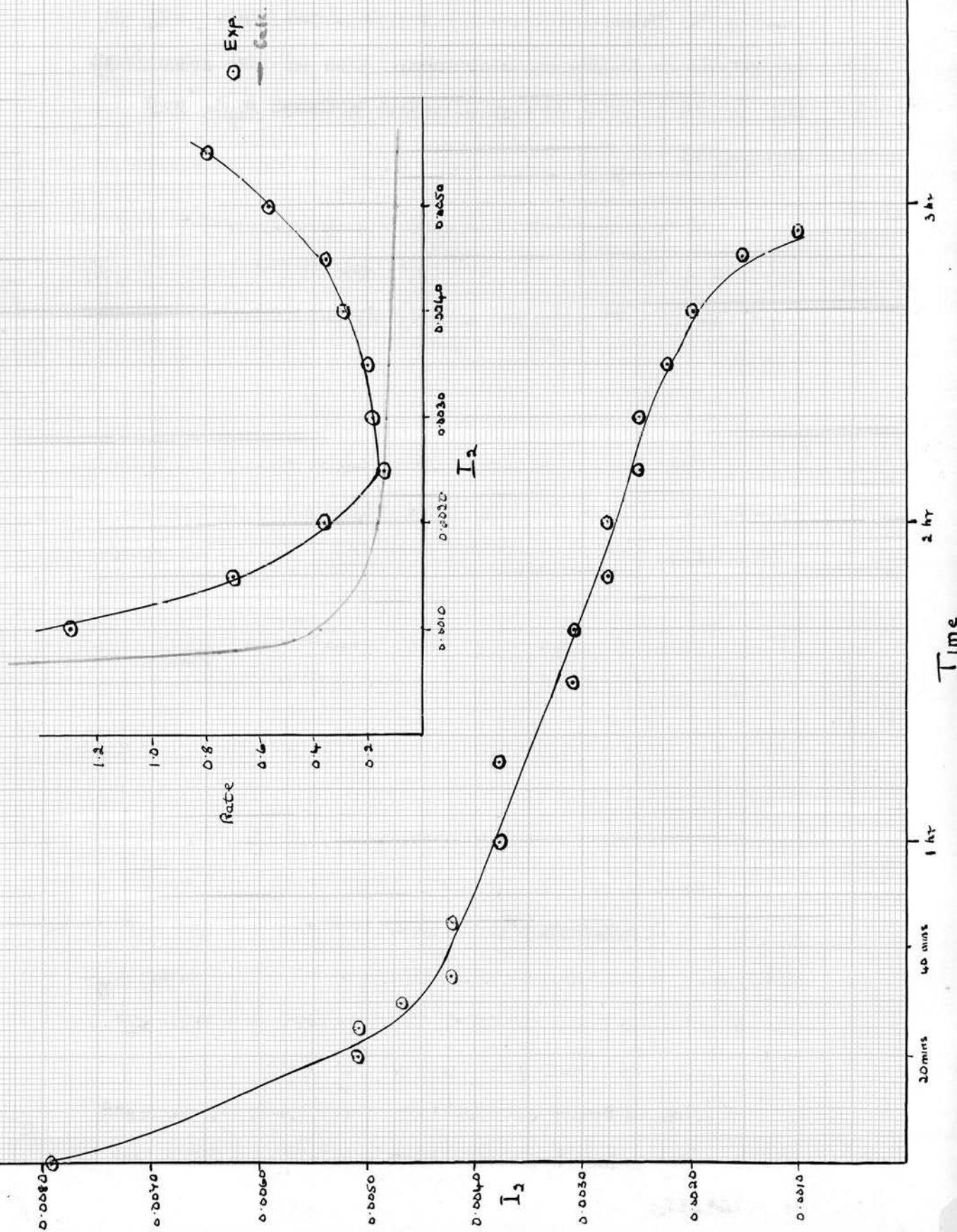


shown. The higher values of a , b and c are nearer the truth in this case. It would seem that the true expression for the rate must take some account of the actual concentrations of the intermediates but this can hardly be done as long as the only means of following the reaction is the colour of the iodine in solution. If allowance for the decrease in phosphorus concentration during reaction is made in Figure XXVIII., a decrease in the calculated values for the rate and a slight shift of the point at which infinite rate should occur, takes place. The decrease is of the order of 6%, 12% and 25% at I_2 0.0050, 0.0030 and 0.0010, and the shift in the point at which infinite rate is reached theoretically is of the order of 0.00010 in the iodine concentration and is in the direction of smaller iodine concentration.

Note on Proposed Mechanism.

It has been suggested that the reason for the sharp initial fall in the rate of reaction is due to the time required for stationary concentrations to be set up. A closer examination of the scheme shows that it includes no reaction which reproduces I_2 molecules and could therefore cause the necessary slowing up of the initial rate. If a large amount of iodine goes to lower iodides the phosphorus concentration may be very much reduced, but /

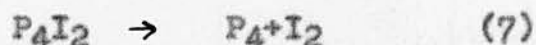
Figure XXVIII



but then the final increase in the rate would not be likely to occur. Various suggestions were made as to how this might be overcome. One of the likeliest was to postulate an equilibrium between P_2I_2 and P_2I_4 thus



This was found to give a kinetic expression totally unrelated to the experimental facts. It was then decided to try making the first reaction reversible.



When the kinetics were worked out with this extra reaction added the same expression as before was obtained with a , b and c altered to a' , b' and c' where

$$a' = \frac{k_2a}{k_2+k_7} \quad b' = \frac{k_2b}{k_2+k_7} \quad \text{and } c' = c.$$

This introduces a reaction which can reproduce iodine and account for the initial slowing up in the reaction rate. The final increase in rate can be accounted for by the accumulation of P_2 and P_2I_2 molecules increasing the chance of the removal of iodine. Other reactions may also be reversible but it is not possible to test this unless other means of following the reactions can be devised.

The effects of moisture was shown to consist partly in a large increase in a or k_1 . With the possibility /

possibility of reaction (being reversible, the action of moisture may be to favour the forward reaction in such a way as to make the back reaction of much less importance.

EFFECT OF ETHER.

The effect of solvents on the reaction has already been shown to be considerable and on page 71 an attempt to make a closer study of the reaction is described. This showed that phosphorus pentoxide may be having some effect on ether but in view of the complicated course followed by the reaction in pure carbon tetrachloride this is in some doubt. Accordingly a series of experiments were carried out using the same initial volumes and concentrations of phosphorus and iodine but varying the amount of ether present. The reactions were carried out in the dark at 15°C. The concentrations of phosphorus and iodine in ~~the~~ moles per litre were

$$P_4 = 0.0058 \quad I_2 = 0.00398.$$

The reactions were carried out using ether purified as described on page 71 and kept over P_2O_5 . The phosphorus and ether solutions were mixed and left over P_2O_5 with frequent shaking for 3 hours and then the iodine was added and the course of the reaction carefully followed.

Results 1. to 4 in Table 22 were obtained in this way the rate at $I_2=0.00200$ being taken as an indication /

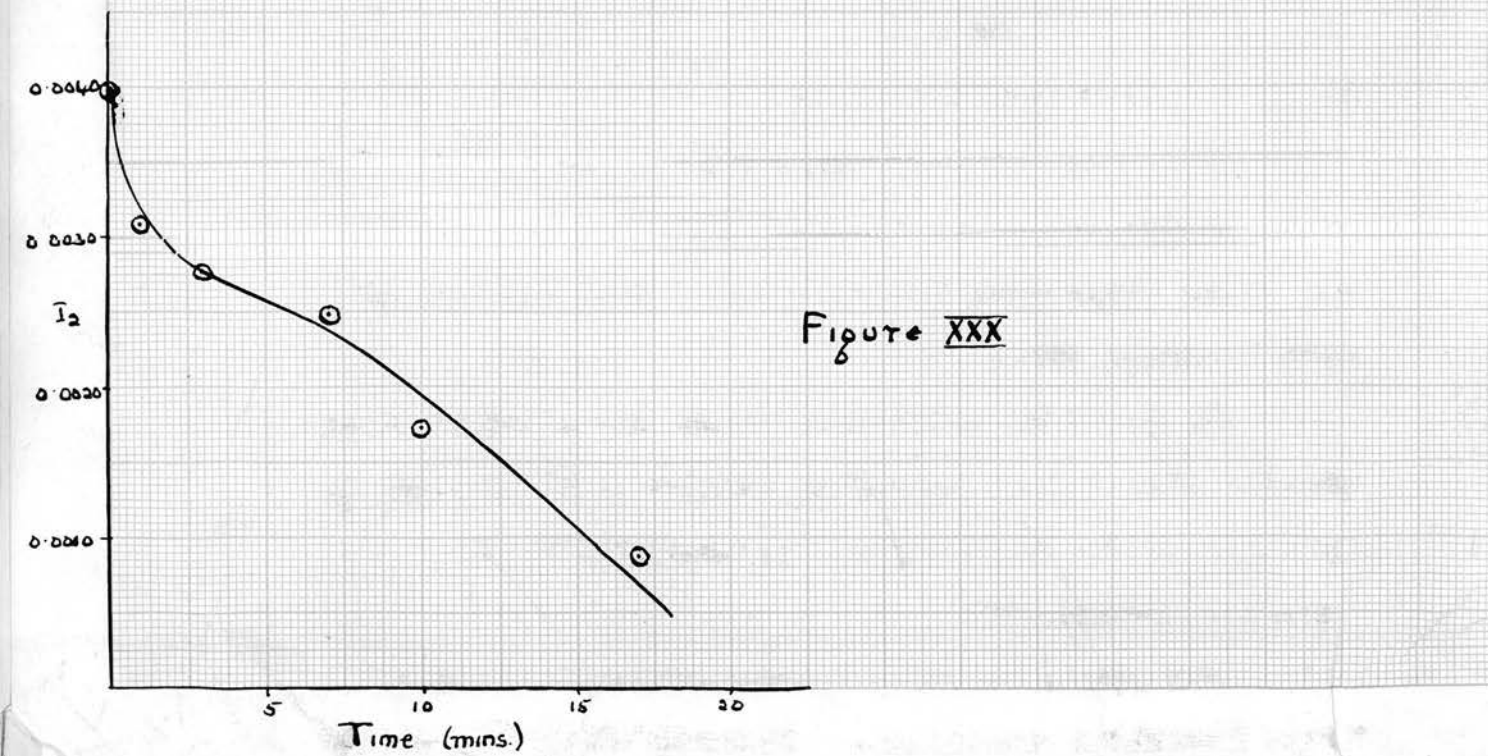
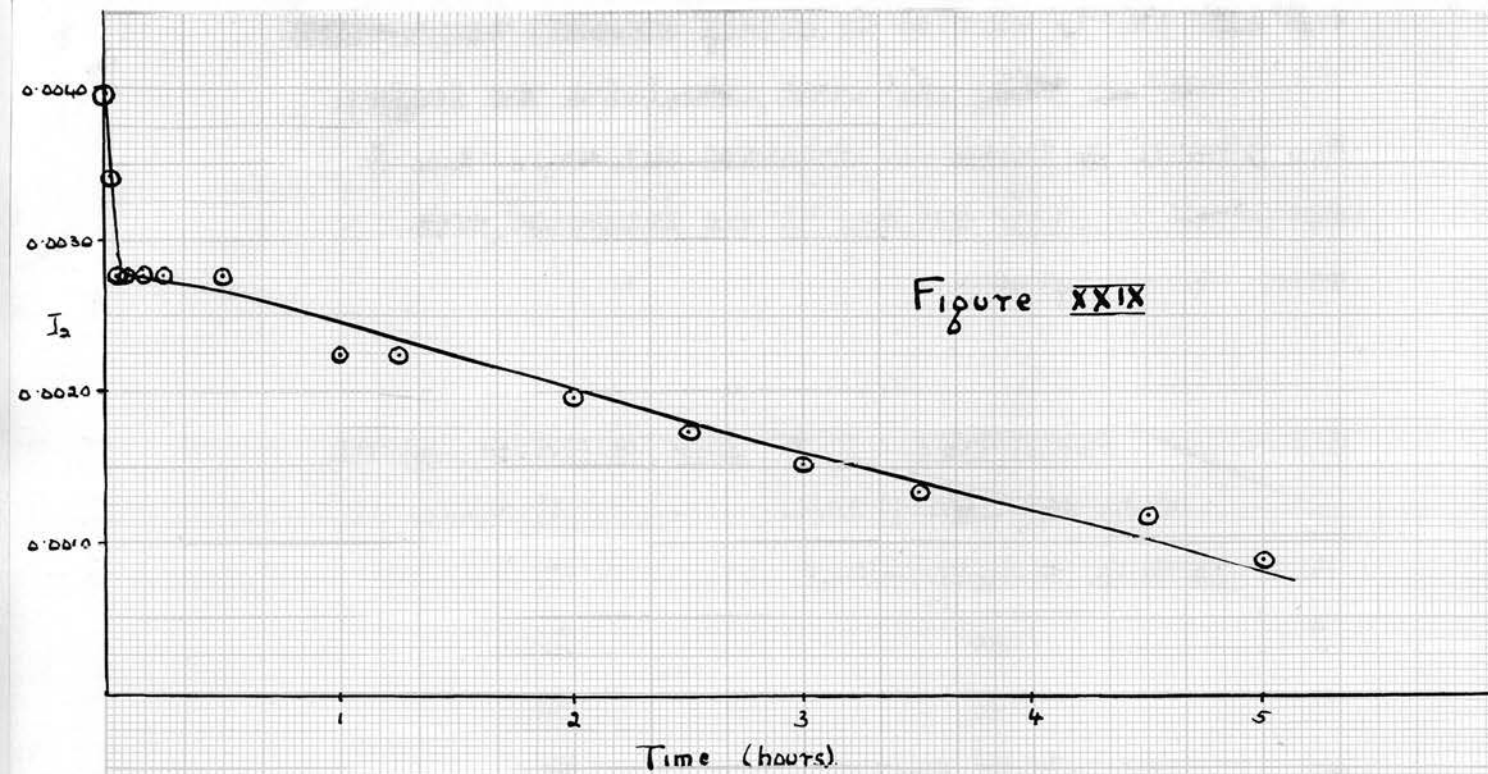
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indication of the rate of reaction. Here little change in rate is shown but when the large increase in rate obtained in the previous qualitative work is remembered it can only be concluded that P_2O_5 is removing the ether.

Some carefully dried ether was left over P_2O_5 and the next day the P_2O_5 had ceased to be loose and powdery. After several days it went slightly brownish and after one month it was black. After ten months the P_2O_5 had been reduced to a black tarry liquid containing some brown lumps which resembled burnt sugar. The ether was decanted off and found to distil at $32 - 33^\circ C$. When water was added to the black mass left in the bottle a slow reaction took place and a very persistent foam was formed. Hence ether is undoubtedly attacked by phosphorus pentoxide.

In an early attempt to eliminate the effect of P_2O_5 , the ether was purified as before and distilled into a dried Woulfe's Bottle. One hole of this contained a calcium chloride tube while the other was fitted with a graduated pipette having a calcium chloride tube on the end. In this way the ether was kept dry and measured volumes could be removed. The same concentrations of phosphorus and iodine as before were used, the phosphorus being the dried stock solution, and the iodine stock solution being kept over P_2O_5 , but no P_2O_5 was introduced into the reaction vessel. At first the ether and phosphorus were added together and /



and left for 15 minutes to attain constant temperature but later the ether was added along with the iodine. No. 5 below in Table was obtained this way. No. 6 contained no ether and No. 11 was saturated with water for comparison.

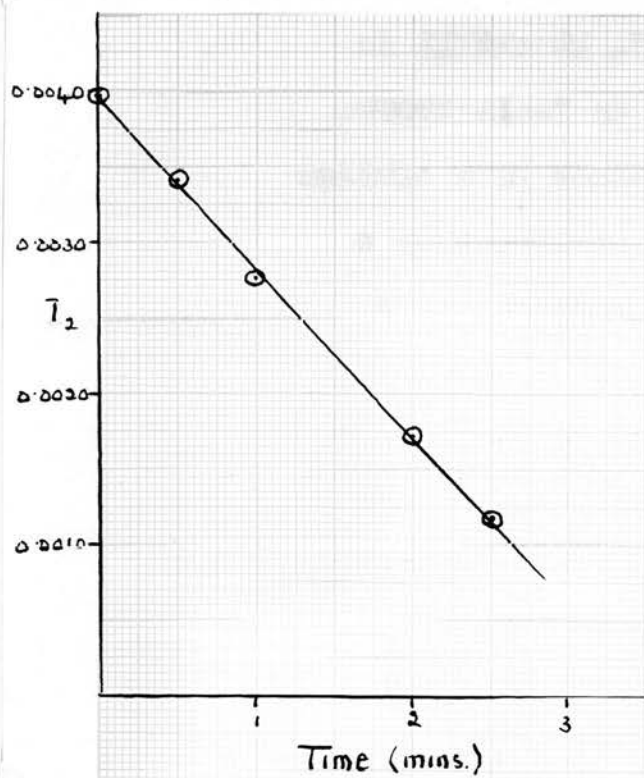
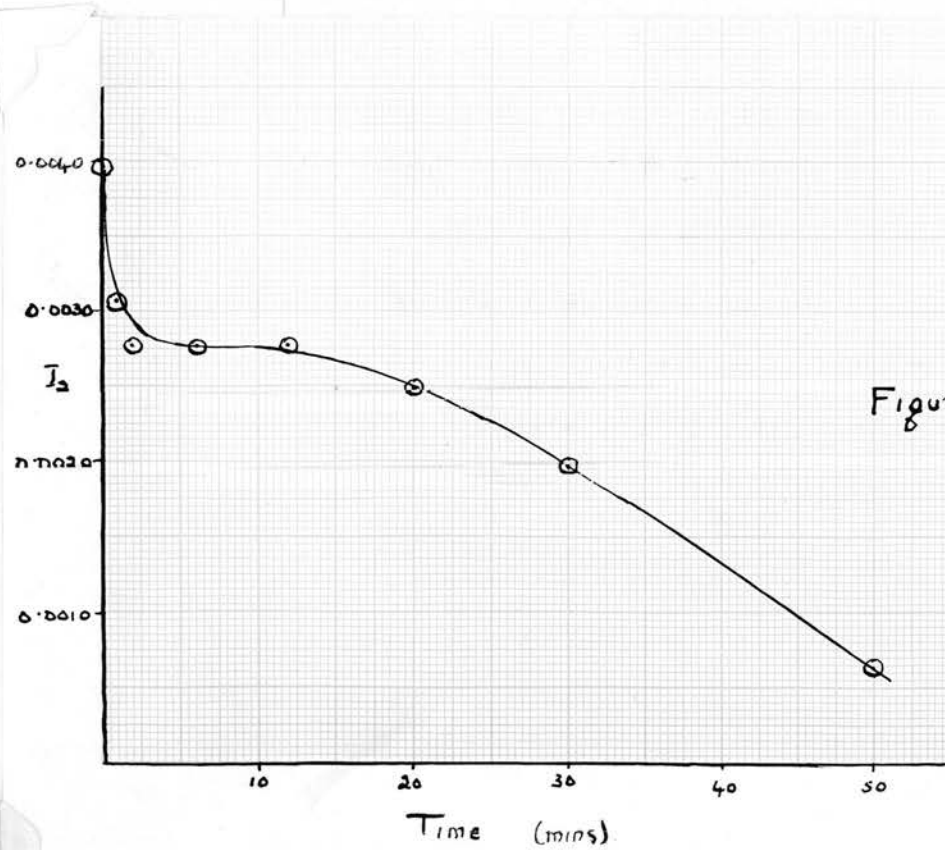
Table 22.

<u>No.</u>	<u>Conditions</u>	<u>Time to change 0.0002</u>
1	P ₂ O ₅ and left 3 hrs.	78 mins.
2	As in 1, + 0.5% ether	63
3	1.5	72
4	2.5	69
5	No P ₂ O ₅ or ether	34
6	No P ₂ O ₅ . 2.5 % ether with P ₄	0.17
7	0.40	I ₂ 1.4
8	0.50	2.1
9	0.75	1.1
10	1.00	0.18
11	Saturated with water	2.8

This shows a very large effect due to ether but owing to the action of P₂O₅ and possibly also P₄ on the ether there does not seem to be much hope of doing more accurate work.

It is to be noted that ether has a larger accelerating effect than solutions saturated with water but this may be due to the great solubility of ether in carbon tetrachloride.

The graphs showing I₂ conc./time for some of these reactions are shown. Figures XXIX, XXX, XXXI,

Figure XXXIFigure XXXII

and XXXII, correspond to Nos. 5, 7, 10 and 11 in Table 22. All the results 1 to 5 in Table wherein little increase in rate had taken place gave similar graphs, but where acceleration was occurring to a large extent the graphs approached more and more closely to being one straight line as is shown in Figures XXX, XXXI, and XXXII. This is in accordance with the suggestion that the action of ether and water, consists in increasing the rate of the initial reaction, thereby diminishing very much the effect of the intermediates and their ability to cause a slowing up in the rate. The rate/ I_2 conc. curve corresponding to Figure XXXI. would be a straight line.

As other solvents would present difficulties similar to those experienced with ether and in many cases of a more serious nature research on the effect of solvents was not continued beyond this point.

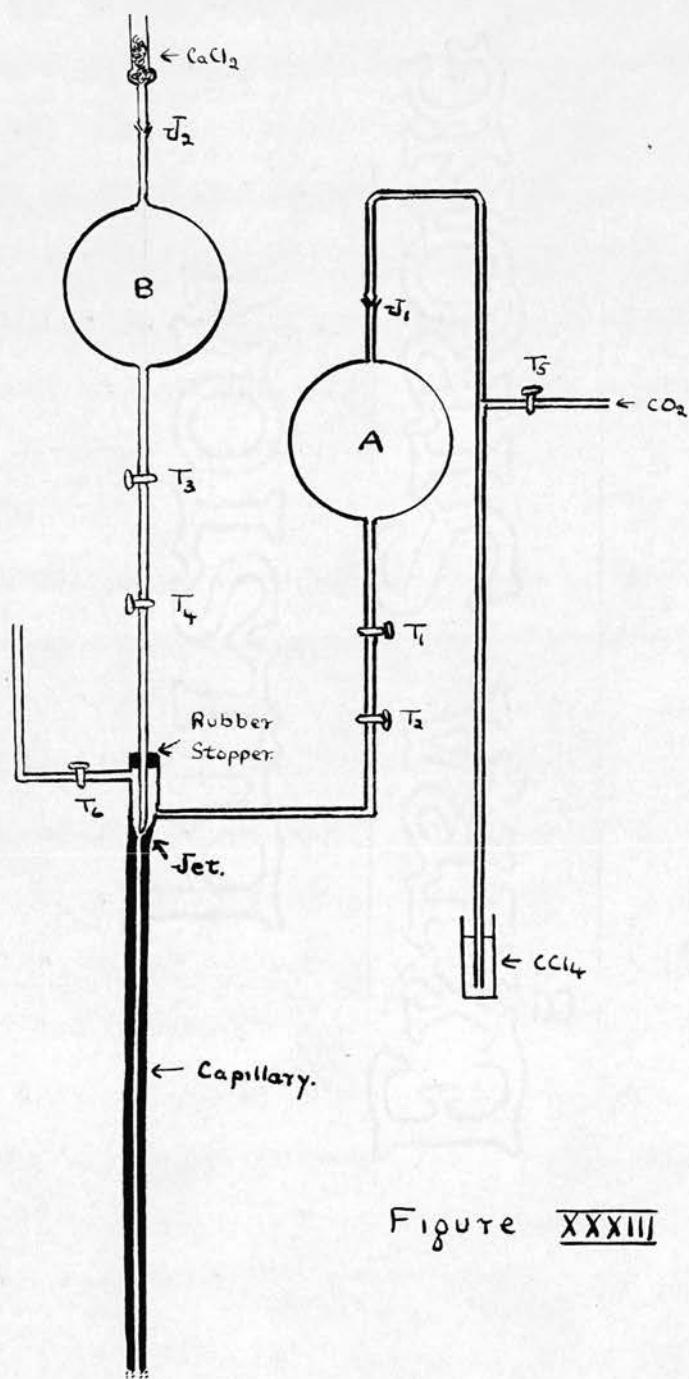
Further, an investigation of the action of light would be liable to necessitate the use of even more complicated equations and so it was decided to pass on to the study of the reaction between phosphorus and bromine.

PHOSPHORUS AND BROMINE IN SOLUTION.

It has long been accepted that when phosphorus and bromine react the tribromide, PBr_3 , is first produced and that with excess of bromine the pentabromide PBr_5 , is obtained. The equilibrium $\text{PBr}_3 + \text{Br}_2 \rightleftharpoons \text{PBr}_5$ has been studied. A heptabromide has been reported but with the concentrations of bromine and phosphorus to be used in the experiments this will never be produced appreciably. Of more importance is the possibility of P_2Br_4 , analagous to P_2I_4 , being formed. Besson and Fournier⁶³ attempted to prepare this compound but with no success and it has never been reported.

Carbon tetrachloride was again used as solvent and P_2O_5 was used as the drying agent. The phosphorus solutions were prepared as before and the bromine solutions were prepared by distilling liquid bromine into carbon tetrachloride and drying the solutions over P_2O_5 . The bromine solutions were determined by shaking portions with aqueous potassium iodide and titrating the iodine released with sodium thiosulphate.

Preliminary experiments were carried out by mixing dried solutions of bromine and phosphorus in stoppered test-tubes in the dark and applying the method used in the iodine experiments. It was found that complete reaction was taking place in less than one second except in cases where the bromine concentration was high enough to take almost all the phosphorus /

Figure XXXIII

phorus to the tribromide. These last took several minutes and could be slightly speeded up by exposure to a 100 watt lamp. This was a light effect not a temperature effect. A further difficulty lay in the fact that before much colour was produced, the bromine solutions had to be more concentrated than the iodine solutions had been. Also, when the bromine solutions were placed in the standard test-tube it was difficult to tell between solutions containing 0.014 and 0.020 moles bromine per litre. Hence the method used in the iodine experiments cannot be used for bromine.

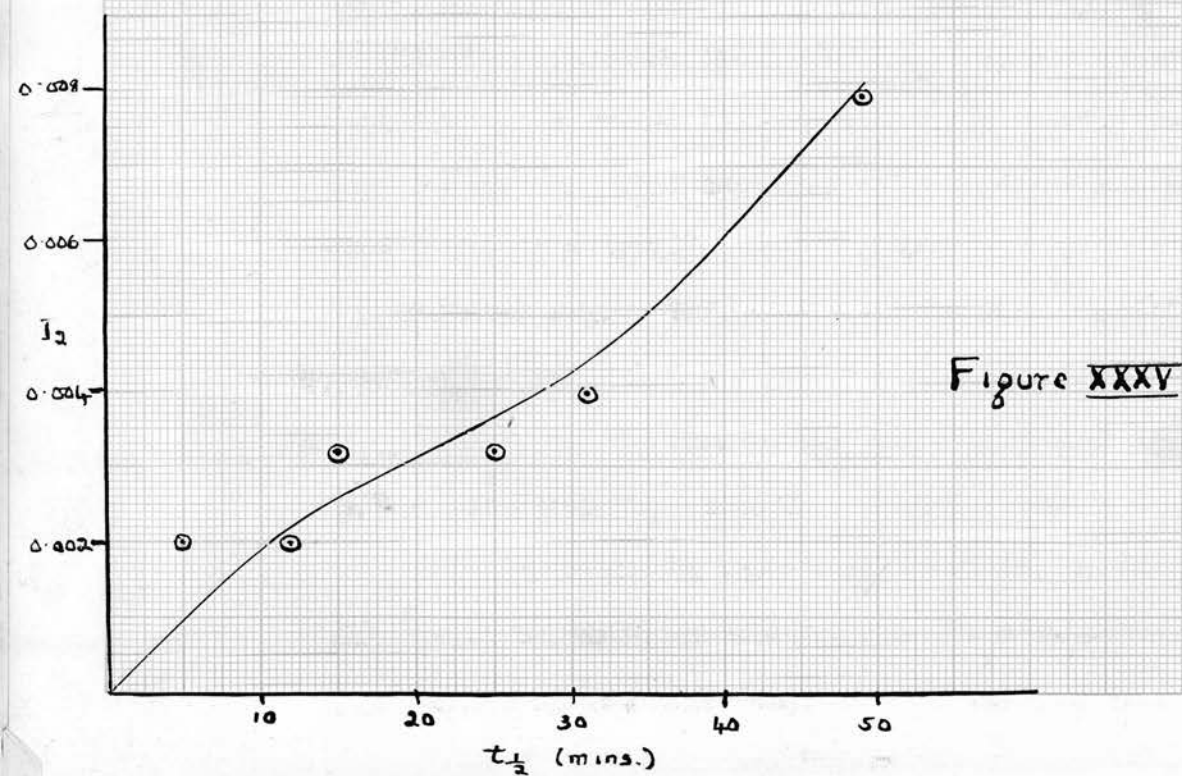
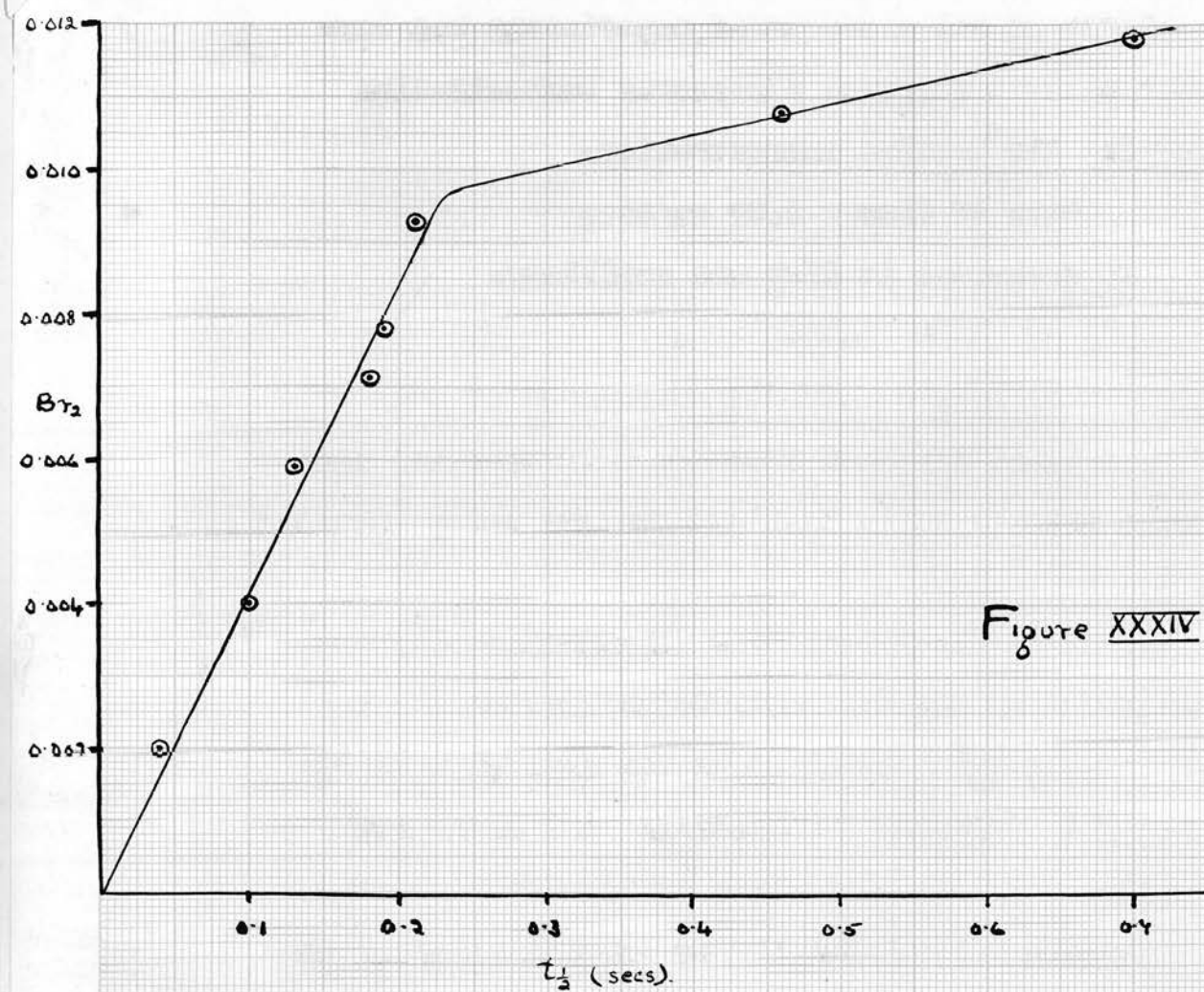
It was decided to use a streaming method in these experiments and the apparatus shown in Figure XXXIII. was constructed. Phosphorus and bromine solutions were kept in A and B which could be filled at the ground glass joints J_1 and J_2 . A calcium chloride tube is fitted at J_2 to keep the bromine solution dry. A pressure slightly above atmospheric is maintained in A by passing in carbon dioxide at T_5 so that a slow stream of gas bubbles out through the carbon tetrachloride vessel shown. A is filled with CO_2 before the phosphorus solution is filtered in. The phosphorus solution flows through T_1 and T_2 and down the capillary. The bromine comes through T_3 and T_4 out through the jet and down the capillary. The solutions could be made to mix completely at the tip of the jet by suitably adjusting its position. The side-tube and tap T_6 were found to be necessary if /

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if the tubes leading from A and B were to be filled with liquid and no bubbles of gas allowed to come down the capillary. These tubes were filled by temporarily closing the foot of the capillary, allowing the solutions to flow until the liquid entered the side-tube, and then blowing them back with CO_2 so that all air bubbles were cleared out of the tubes. If this were done carefully no liquid flowed back from beyond the jet into A or B. A was blackened to prevent light acting on the phosphorus.

By suitably adjusting T_1 and T_3 the same rate of flow down the capillary, giving the same proportions of A and B, could be obtained every time T_2 and T_4 were opened. The proportion of solutions from A and B could be found by determining the bromine in B with aq HI and $\text{Na}_2\text{S}_2\text{O}_3$ and then finding the concentration of bromine coming down the capillary with CCl_4 alone in A. The concentration of phosphorus in the liquid coming down the capillary was found by collecting it and determining the total phosphorus by the method used in the iodine experiments. The bore of the capillary was obtained by weighing the mercury contained in a known length of it. The rate of flow was found with a stop-watch and a measuring cylinder. The point at which the bromine concentration had been reduced to any value could be found by holding a piece of similar capillary, containing a solution of the required concentration, alongside the stream of liquid and matching the colour.



First of all a series of experiments was carried out using a constant phosphorus concentration and varying the bromine concentration.

Rate of flow = 2.00 cc/sec.

1 cc contained in 25.9 cms capillary.

∴ 1 cm = 0.0193 sec.

P_4 conc = 0.0018 moles/litre.

The times for half reaction were obtained with different bromine concentrations and are shown graphically in Figure XXXIV.

In these experiments the illumination was always provided by the same artificial lighting. In Figure XXXV. results obtained in the dark with iodine and constant phosphorus ($P_4=0.0163$) are shown for comparison. The concentration of bromine and iodine are comparable but the phosphorus concentration in the bromine experiments is about a tenth of that in the iodine experiments. The rate of reaction in the bromine experiments is about 2000 times that in the iodine experiments. The bromine results can be described as lying on two straight lines intersecting at $Br_2 = 0.0097$. But at $Br_2 = 0.0102$ there is enough bromine to take all phosphorus to $P Br_3$ so this change in slope of the graph may be caused by the coming into play of the $P Br_3 + Br_2 \rightleftharpoons P Br_5$ equilibrium. The iodine results can best be rendered as a curve.

Examination of the colour of bromine down the capillary during any one experiment did not show any sign /

sign of any sudden change in rate of reaction similar to that shown by the iodine reaction, but this could not be definitely established owing to the difficulty in detecting a small change in bromine concentration.

Next an examination was made of the effect of different solvents.

64

Child and Walker recently examined the continuous absorption spectrum of bromine in solution and found a displacement of the bands, in those solvents which give brown solutions with iodine. Hence it was thought that a solvent effect might appear in the phosphorus bromine reaction. To test this experiments were carried out with $P_4=0.0018$ and $Br_2=0.0070$ and the various solvents introduced by dissolving the bromine in carbon tetrachloride plus known amounts of a second solvent. The results are given in Table 23 the concentrations being given as the concentrations in the capillary as was done in the previous results.

Table 23.

<u>Solvent introduced</u>	<u>Distance for half reaction</u>
None	9.0 cms.
3% carbon disulphide	9.5
3% hexane	9.0
3% ether	8.0
3% acetone	acetone reacted with the bromine
Saturated with water	8.5

This shows that there is little solvent effect in the bromine reaction.

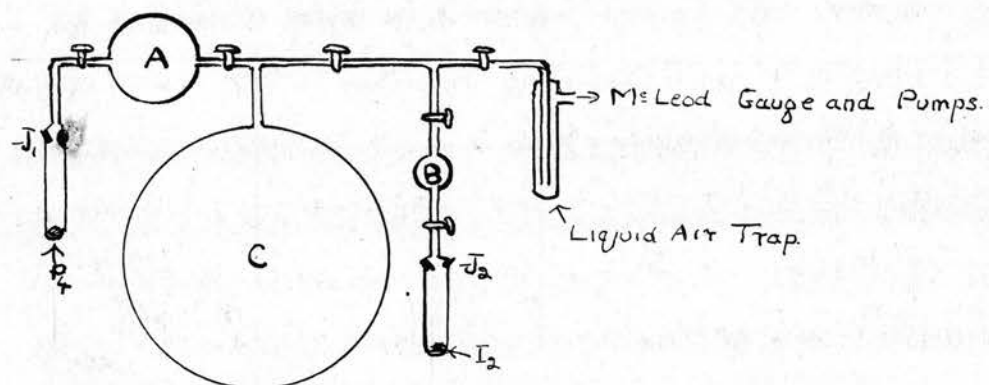
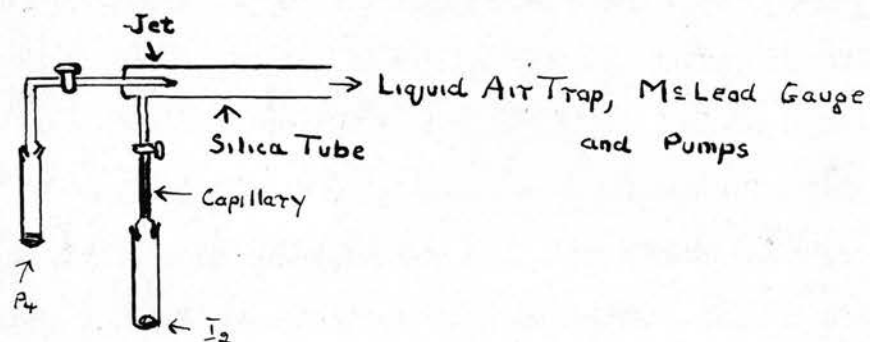
A series was taken with $\text{Br}_2 = 0.0070$ and varying phosphorus from 0.0020 up to 0.040. Owing to the rubber stopper swelling during the course of the experiments and thus changing the position of the jet and altering the mixing, this series was not accurate enough to be shown here but in spite of the great range of phosphorus concentration used the increase in rate with increasing phosphorus was not very far from being linear. There was definitely no increase in rate comparable with that experienced with dry solutions of iodine and phosphorus, and increasing phosphorus concentration of Figure XVII.

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From these results it is not possible to formulate any definite mechanism for the phosphorus bromine reaction, but the reaction must consist of a series of several reactions and probably involves a series of reactions similar to that suggested for phosphorus and iodine. In this case however reaction is much faster and much less affected by light and solvents, hence it may be expected to be similar to the reaction between phosphorus and iodine in the presence of ether or water, and may depend mainly on the rate of the initial reaction. In this connection the difference between the two curves in Figure XVII may be noted, and also the increasing smoothness of reaction with increasing ether described on pages 93 to 96.

Since chlorine would be expected to give^a much faster reaction, and one even more difficult to follow than /

than that with bromine, no attempt was made to study the reaction between phosphorus and chlorine in solution.

Figure XXXVIFigure XXXVII

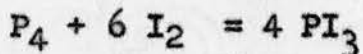
PHOSPHORUS AND THE HALOGENS IN THE GASEOUS STATE.

To test the possibility of observing the reaction between phosphorus and iodine the apparatus shown in Figure XXXVI. was constructed. The phosphorus (white) and iodine reservoirs were attached by the ground glass joints J_1 and J_2 . The whole apparatus could be exhausted down to a pressure of 0.001 m.m. mercury by means of a mercury vapour pump backed by an oil pump. A McLeod Gauge was used to read off the pressure of residual air and a liquid air trap was inserted to protect the pumps and gauge from phosphorus and iodine. After the apparatus had been exhausted phosphorus and iodine vapours were introduced into the five litre bulb C by means of the taps and the small bulbs A and B. Since the vapour pressure of phosphorus is about a tenth of that of iodine the capacity of A was ten times that of B (500 cc to 50 cc). No sign of reaction between phosphorus and iodine was seen in any part of the apparatus either in the dark or in presence of strong light. On leaving the apparatus in the dark for two days some bright red specks which did not volatilise or change in any way on being gently heated were found on the walls of C and in the tubes. These were probably red phosphorus,

The apparatus was now modified to that shown in Figure XXVII and a stream of phosphorus and iodine vapours /

vapours were drawn from the reservoirs by the pump. The capillary was inserted to cut down the vapour pressure of the iodine. It was hoped that reaction would occur at the tip of the jet but no luminiscence or deposit was obtained in any part of the silica tube, in the light or in the dark, in the cold or when the tube was heated to a dull red. After the experiment iodine and red phosphorus were found in the liquid air trap. Bromine was substituted for iodine and the only result was that the bromine tended to enter the phosphorus reservoir and react with the solid phosphorus. Since there was no luminiscence nor any deposit, and because the vapour pressures were so very low, it would be very difficult to study the reactions in the vapour state.

At this point some experiments carried out by ⁶⁵ Pélabon may be mentioned. He was interested in the "volatility product" and stated that



then he wrote $(P_4) (I_2)^6 = K (PI_3)^4 = A.$

He holds that since the vapour pressure of solid PI_3 is constant A is also constant and the solid PI_3 will only be deposited when the vapour pressures of P_4 and I_2 are large enough to give a certain value for A .

He took a tube 50 cms long, evacuated it, and left it in the dark with white phosphorus at one end and iodine at the other. After several days crystals of /

of PI_3 appeared at either end of the tube but none were obtained in the centre. When the centre of the tube was reduced to a capillary crystals only appeared in the capillary. With a plug of degassed charcoal in the tube the crystals appeared on the iodine side of the plug midway between it and the iodine. When the tube was filled with hydrogen, crystals appeared in every part of the tube. These experiments only succeeded with thoroughly dried tubes and P_2I_4 was never obtained.

He states that in the first experiment it is only at the ends of the tube that A can attain the required value. With the capillary present he holds that the capillary offers such a resistance to the passage of vapour that the volatility product reaches the value A at that region. With the charcoal present, he ascribes the presence of deposit on the iodine side of the plug only to the complete absorption of iodine but not phosphorus vapour by charcoal. His explanation of the last experiment is that hydrogen dissolves iodine readily and thus aids the attainment of pressure A.

It would seem to be much more likely that the hydrogen acts as a third body in promoting reaction and that the narrow capillary has a similar effect.

An attempt to study the reaction with chlorine was made and the apparatus shown in Figure XXXVIII. was devised. White phosphorus was contained in a boat B in a tube about 2 cms wide. The apparatus

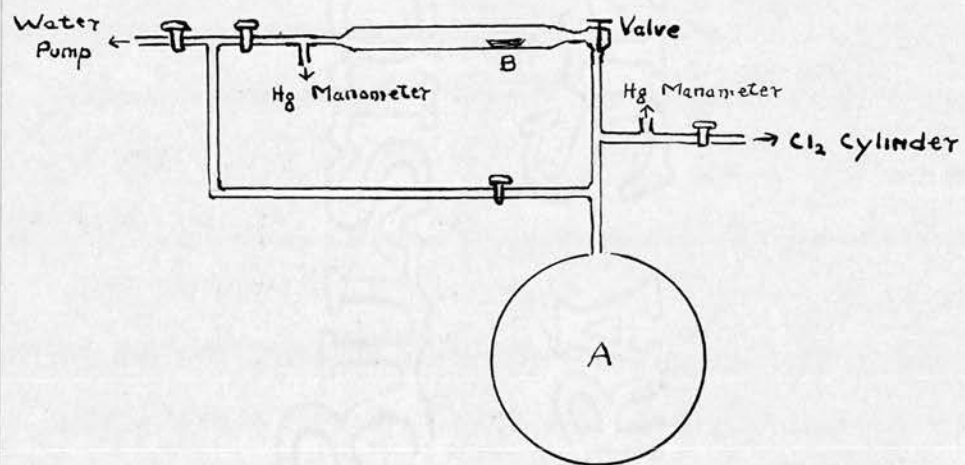


Figure XXXVIII

was exhausted by a water pump and the 2 litre bulb A was then filled with chlorine. The valve was opened and a stream of chlorine allowed to pass over the phosphorus. Copious white fumes were given off and as the rate of flow of chlorine was increased the phosphorus liquified and finally evaporated rapidly. At this stage a glow was seen in the tube above the boat. This glow could not be drawn along the tube by the water pump and appeared when the pressure given by the manometer at the end of the tube was about half an atmosphere. Shutting off the chlorine extinguished the glow immediately. After the experiment a copious deposit of PCl_5 was found all along the tube. The glow was probably due to reaction between chlorine and phosphorus vapour, and it would not travel far from the phosphorus since so much chlorine would be coming past the phosphorus that all the phosphorus vapour would be removed before it could travel any distance.

A tube containing liquid bromine was substituted for the bulb containing chlorine. On opening the valve bromine vapour passed into the tube, but even ^{and} with the valve full open/the bromine heated to boiling, no great pressure of bromine reached the manometer. The phosphorus was also heated, but it was found impossible to create a visible glow. A dense yellow deposit, turning reddish later, was formed at the end of the tube next the bromine whilst at the other side of the phosphorus a colourless fuming liquid collected.

Both these dissolved in water. Presumably the solid was PBr_5 and the liquid PBr_3 , enough phosphorus being present to react with all the bromine as it entered.

These experiments show that an investigation of the kinetics of the gaseous reaction would involve very great difficulties.

S U M M A R Y.

1. A method has been developed for estimating free phosphorus in organic liquids.
2. The use of a photocell to follow the phosphorus iodine reaction in solution does not give a satisfactory method due to the sensitiveness of the reaction to light. Both red and green lights have a large accelerating effect.
3. The absorption of light P_2I_4 in CCl_4 has been compared with that given by I_2 in the same solvent.
4. Analytical methods of following the P_4-I_2 reaction were tried and very great difficulties encountered. The reaction was finally studied by direct visual comparison of the iodine colour with standards.
5. The reaction between P_4 and I_2 in solution goes to completion if sufficient P_4 is present to take all I_2 to P_2I_4 , but the rate varies greatly with the conditions.
6. There is little temperature or surface effect.
7. The reaction is greatly favoured by those solvents which give brown solutions with iodine, but accurate comparison is difficult due to reaction between the solvents and P_2O_5 .
8. A series of experiments have been carried out with the same I_2 concentrations and different P_4 concentrations using both wet and dry solutions. The rate of reaction has been plotted against P_4 concentration and a reaction mechanism suggested. This scheme fits the curves satisfactorily.

9. Using the same P_4 concentrations and dry solutions I_2 concentrations have been plotted against rates of reaction. Values for the rate calculated from the previous scheme give curves of the required shape but which only approximately fit the experimental curves. Probably the true expression must take account of the concentration of intermediates.

10. Some results have been obtained in presence of ether. The reaction proceeds at a more uniform pace in this case. Probably forward reactions are favoured at the expense of back reactions. There are indications that moisture acts in a similar manner.

11. The $P_4 - Br_2$ reaction has been studied in dry CCl_4 solutions using a streaming method, as it was not possible to study the dark reaction, illumination of constant intensity was used.

12. There is little increase in rate in presence of those solvents which give brown solutions with iodine.

13. The reaction is 2000 times faster than that with I_2 in the dark using dry CCl_4 solutions. It seems to proceed at a fairly uniform rate and is probably similar to the ether catalysed I_2 reaction.

14. The low vapour pressures of the reactants make the study of the reactions between phosphorus and the halogens in the gaseous state very difficult. No glow was ever seen unless when chlorine was passed over solid white phosphorus.

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